Relative Migratory Aptitudes of Doubly and Triply Bonded Groups in a Cycloheptatriene System

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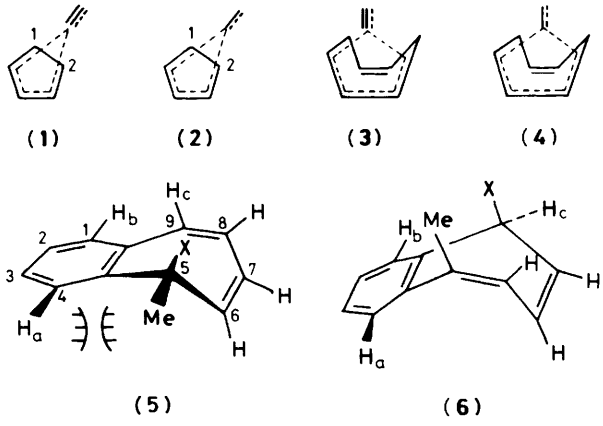
In cyclopentadiene systems, 1,5-shift of triply bonded groups is much slower than that of doubly bonded groups, whereas in the cycloheptatriene systems (**34**) and (**29**), as well as in (**21**) and (**19**), CN and CHO groups have very similar migratory tendencies. In compound (**31**) the C≡CCOPh group migrates to give (**38**; X = C≡CCOPh, Y = H) at 60 °C, whilst the related olefin (**20**) fails to rearrange at 80 °C, and undergoes intramolecular Diels–Alder reaction to afford tetracycle (**40**) at 100 °C. The simple acetylene (**23**) rearranges to a mixture of products (**24**) and (**39**; X = C≡CH, Y = H) at 145 °C. The order of migratory aptitude CHO > COMe > CO_2Me observed in indenes is preserved in the benzocycloheptene system. The aldehyde (**19**) rearranges to (**38**; X = CHO, Y = Br) at 114 °C, the acetyl compound (**22**) gives a little of the 1,5-shift product (**38**; X = $COCH_3$, Y = Br) but mainly the naphthalene (**43**) at 175 °C, whilst the ester (**17**) gives mainly tricycle (**44**) rather than a product of 1,5-CO_2Me shift at 205 °C. The overall migratory order for the cycloheptatriene system; CHO > C≡N, C≡CH > COMe > CO_2Me > alkyl, shows a promotion of the triply bonded groups consistent with variations of strain in the bridged transition states (**1**) compared with (**2**) and (**3**) compared with (**4**).

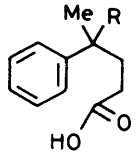
In the preceding paper[1,2] it was firmly established that triply bonded groups (C≡N, C≡CR) participate much less readily than doubly bonded groups [CHO, (*E*)-CH=CHR] in 1,5-sigmatropic shifts about a cyclopentadiene ring. An explanation was suggested based upon the greater strain in a bridged transition state (t.s.) (**1**) for acetylene migration than in the t.s. (**2**) associated with vinyl migration; structure (**1**) resembles a methylenecyclopropane and (**2**) the more stable cyclopropane ($\Delta\Delta H$ 13.6 kcal mol^{-1}).* From this and alternative explanations of the effect[1] it appeared that slower migration of triply than doubly bonded groups would be most keenly felt when t.s. bridging involved formation of a 3-membered ring. For a 1,5-shift about a cycloheptatriene the 'extra' ring present in the t.s. (**3**) for acetylene migration resembles methylenecyclopentene, whilst the t.s. (**4**) for vinyl migration incorporates a cyclopentene moiety. Since methylenecyclopentane and cyclopentane have similar stability[3] the migratory aptitude of doubly and triply bonded groups about a cycloheptatriene might be relatively free of ring-strain effects and should reflect more accurately the electronic factors influencing migratory aptitude. To determine migratory aptitudes over the cycloheptatriene framework we selected benzocycloheptenes which would be less likely to react as norcaradiene tautomers[4] than would simple cycloheptatrienes. As shown in structure (**5**) a 5,5-disubstituted benzocycloheptene is destabilised by *peri*-like interaction of a C-5 substituent with an *ortho*-proton (H_a) of the benzo group. 1,5-Shift of X in structure (**5**) relieves this interaction [the C–Me bond in the product (**6**) forms an angle of *ca.* 45° with the C–H_a bond] replacing it by *peri*-like interaction of H_b with H_c. Accordingly any equilibrium between (**5**) and its 1,5-shift product (**6**) should favour the latter and so enable ready observation of the 1,5-shift.

Synthesis of Benzocycloheptenes.—The acids (**7**) and (**8**), readily available *via* Michael addition to acrylic acid derivatives,[5] were readily transformed into tetralones (**9**) and (**10**). As was already known,[5] acid (**7**) gave acid (**9**) upon treatment with sulphuric acid. Friedel–Crafts cyclisation of the acid chloride from nitrile (**8**) ($AlCl_3$, CS_2) gave compound (**10**) in high yield.

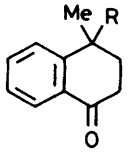


Tetralone (**11**) was smoothly converted into the enol silyl ether (**12**) which afforded the dibromocarbene adduct (**13**) [$PhHgCBr_3$, $(CH_2OMe)_2$]; adduct (**13**) underwent smooth ring-expansion to give compound (**14**) upon silver ion-catalysed[6] rearrangement. Sodium borohydride reduction of ketone (**14**) proceeded cleanly only in the presence of cerium trichloride[7] to give a mixture of the alcohol (**15**) and lactone (**16**). Since both compounds (**15**) and (**16**) gave the cycloheptatriene (**17**) with boiling methanolic hydrogen chloride, it was convenient on a large scale to submit the total product from reduction to acid-catalysed dehydration to give compound (**17**) in 58% yield from ketone (**14**). The ester (**17**) was reduced to the alcohol (**18**) (Bu^i_2AlH, Et_2O), which on Swern oxidation gave the aldehyde (**19**). The actetylene (**23**) was prepared from compound (**19**) by dibromomethylenation (PPh_3, CBr_4) and reaction with Bu^nLi; halogen–metal exchange at the benzocycloheptene C-8 accompanies production of the acetylene. Surprisingly, the acetylene (**23**) (62%) was accompanied by 15% of the isomer (**24**). Since compound (**23**) is recovered unchanged after similar treatment with Bu^nLi, the isomer (**24**) may arise from the carbenoid (**25**) by an anion-accelerated 1,5-shift

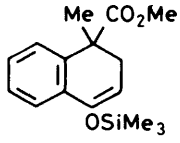
* 1 kcal = 4.184 kJ.



(7) R = CO_2H
(8) R = CN



(9) R = CO_2H
(10) R = CN
(11) R = CO_2Me



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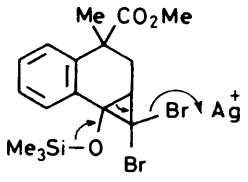

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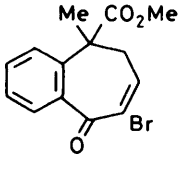

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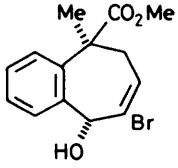

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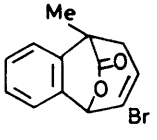

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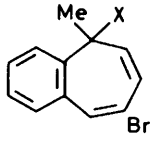
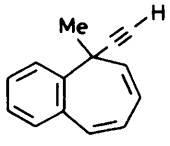


(17) X = CO_2Me
(18) X = CH_2OH
(19) X = CHO
(20) X = (*E*)-CH=CH COPh
(21) X = CN
(22) X = COMe

[structure (**25**), arrows] to give compound (**26**) which then loses hydrogen bromide in the normal way. Alternatively, formulation of intermediate (**25**) as (**27**) allows formation of compound (**24**) to be written as a reaction of a 'foiled' carbene [structure (**27**), arrows].



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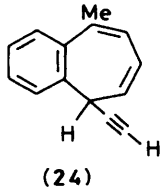

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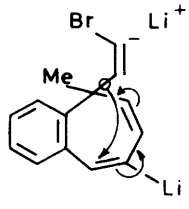

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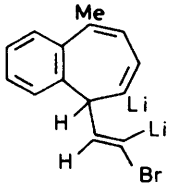

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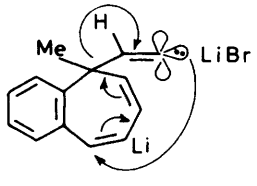
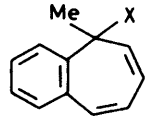


(27)

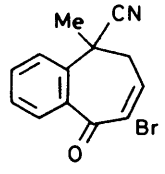
Reaction of the bromide (**18**) with Bu^{n}Li, followed by aqueous quench, gave the debrominated product (**28**) which was converted *via* aldehyde (**29**) into dibromomethylene compound (**30**). Reaction of dibromide (**30**) with Bu^{n}Li also gave both acetylenes (**23**) (70%) and (**24**) (16%). The nuclear bromine in the dibromomethylene derivative of aldehyde (**19**) is therefore without effect upon the formation of the acetylene (**24**). The acetylene (**23**) available by these two routes was readily converted into the benzoyl derivative (**31**) by reaction with PhCOCl, Et_3N, $PdCl_2 \cdot 2Ph_3P$ (cat.), and CuI (cat.).



(28) X = CH_2OH
(29) X = CHO
(30) X = C=CBr_2
(31) X = C≡CCOPh
(32) X = CH=CH_2
(33) X = (*E*)-CH=CHPh
(34) X = CN
(35) X = COPh

The aldehyde (**29**) was converted into the olefins (**32**) and (**33**) by Wittig reactions with methylene- and benzylidene-triphenylphosphorane, respectively. Reaction of aldehyde (**19**) with the sodium salt of diethylphosphonoacetophenone [diethyl (2-oxo-2-phenylethyl)phosphonate] gave the (*E*)-benzoylvinyl compound (**20**).

The aldehyde (**29**) was converted into its oxime, which with boiling acetic anhydride gave the nitrile (**34**) albeit in poor yield (25%). The nitrile (**21**) was available from the tetralone (**10**) *via* the enol silyl ether, addition of dibromocarbene, and silver ion-catalysed ring expansion to ketone (**36**). Reduction of ketone (**36**) ($NaBH_4$, $CeCl_3$) gave the alcohol (**37**) (60%) as well as the lactone (**16**) (15%). Reaction of (**37**) with Ph_3P–CBr_4 and treatment of the crude product with 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) gave nitrile (**21**) in 41% yield from alcohol (**37**). The ketones (**35**) and (**22**) were prepared from the appropriate aldehyde and Grignard reagent followed by oxidation.



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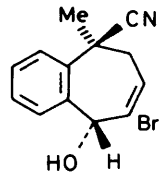


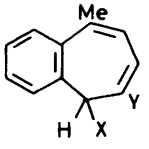
(37)

Thermolysis of Benzocycloheptenes.—Thermolyses of the benzocycloheptenes were conducted in degassed solvents and were followed by 90 MHz FT ^{1}H n.m.r. measurements. For the compounds in the Table, rearrangement proceeded cleanly to give the products (**38**) of a simple 1,5-shift of X, and/or the products (**39**) derived from them by 1,5-hydrogen migration. The activation parameters and solvent rate effects (Table) support the occurrence of concerted 1,5-shifts, as does our failure to observe cross-over products when compounds (**21**) and (**29**) rearrange together.

Acetylene and nitrile migrations occur readily in the cycloheptatriene system; the benzoylacetylene (**31**) rearranges at 60 °C, and the simple acetylene (**23**) rearranges at 145 °C (210 min) to give mainly compound (**39**; X = C≡CH, Y = H). The

Table. Product and rate data for thermolyses

Compound	Product(s)	$10^4 k/s^{-1}$ (t/°C) (solvent)	$\Delta' S^{\ddagger}$/cal K^{-1} mol^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}
(19)	(38; X = CHO, Y = Br)	0.499 (114.4) 1.83 (127.1) 4.56 (138.7) 8.47 (147.1) (C_6D_6)	−8.6 ± 2.7	27.16 ± 1.1
(21)	(38; X = CN, Y = Br) and (39; X = CN, Y = Br)	0.473 (137.2) 1.20 (148.3) 2.64 (159.6) 5.97 (169.4) (C_6D_6) 3.31 (159.6) (CD_3CN) 5.84 (159.6) (CD_3OD)	−12.7 ± 1.8	27.2 ± 0.8
(29)	Mainly (39; X = CHO, Y = H)	2.25 (138.1) (C_6D_6 3.42 (138.1) (CD_3CN)		
(34)	Mainly (39; X = CN, Y = H)	0.392 (138.1) (C_6D_6)		
(31)	(38; X = C≡CCOPh, Y = H) At 139 °C this gives (39; X = C≡CCOPh, Y = H)	0.358 (60.6) 0.937 (69.7) 2.55 (80.1) 8.35 (94.2) (C_6D_6) 3.70 (69.7) (CD_3OD)	−12.7 ± 1.1	22.1 ± 0.4



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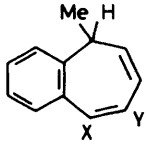

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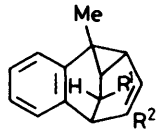
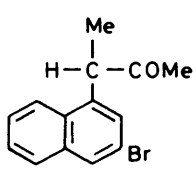


(40) R^1 = COPh, R^2 = Br
(41) R^1 = R^2 = H
(42) R^1 = Ph, R^2 = H

latter product is obtained upon heating compound (**24**) at 130 °C (170 min). It is clear that in the cycloheptatriene system, triply bonded groups compete favourably with doubly bonded groups that showed vastly superior migratory ability about cyclopentadiene systems.[1,8,9] Thus rearrangement of the nitrile (**21**) is only slightly slower than rearrangement of the aldehyde (**19**) (Table), and the olefin (**20**) is unchanged at 80 °C (30 min), indicating slower rearrangement than observed for the acetylene (**31**). Heating the olefin (**20**) at 100 °C (45 min) gives the product (**40**) of an internal Diels–Alder addition. Similar products (**41**) and (**42**) were obtained by heating the olefins (**32**) (100 °C, 7 h) and (**33**) (90 °C, 4.5 h). The 400 MHz ^{1}H n.m.r. spectra of these compounds are very similar to that reported[10] for compound (**41**; H replacing Me).

The order of migratory aptitude CHO > COMe > CO_2Me observed in indenes[8] is maintained in the cycloheptatriene system; aldehyde (**19**) rearranges at 114 °C whereas ketone (**22**) requires heating at 175 °C (110 min) for complete conversion into a mixture of compound (**38**; X = COMe, Y = Br) and two naphthalenes tentatively identified as compound (**43**) and a positional isomer. Rearrangement of the ester (**17**) required heating at 205 °C (2 h) to give tricycle (**44**) rather than a product of 1,5-CO_2Me shift. Thermolysis of the benzoylbenzocycloheptene (**35**) at 160 °C (*ca.* 5.5 h) gave the naphthalene (**45**).



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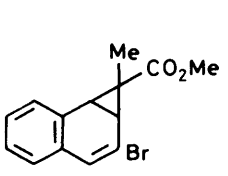

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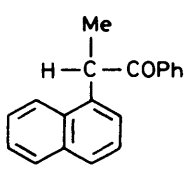

(45)

Migratory aptitudes in the cycloheptatriene system follow the order CHO > CN, C≡CH > COMe > CO_2Me > alkyl. The improved position of the triply bonded groups in this order compared with that prevailing for the cyclopentadiene system[8] would be expected from the variations of strain in the bridged t.s.s (**1**) compared with (**2**), and (**3**) compared with (**4**). The 1,5-migrations of CN about the cycloheptatrienes described here support the earlier work of Ciganek where concerted 1,5-migration about cycloheptatrienes and a benzocycloheptene was proposed.[11]

Experimental

For general comments see preceding paper.[1] Unless otherwise stated all ^{1}H n.m.r. spectra described herein were run at 90 MHz using a JEOL FX90Q or a Perkin-Elmer R32 instrument. 400 MHz spectra were obtained on a Bruker WH-400 instrument at Sheffield University. All thermolyses were carried out in sealed tubes in degassed (five freeze–pump–thaw cycles) solvents. In all cases Me_4Si (typically 1—3 μl) was present as an internal standard. Tubes used for thermolyses (internal diameter 2 mm) were pre-soaked in KOH solution (1—2M) then carefully rinsed successively with distilled water (× 5) followed by A.R. acetone, and dried in an oven at 110 °C overnight. The abbreviation 'wffs' stands for 'with further fine splitting.'

Methyl 1,2,3,4-Tetrahydro-1-methyl-4-oxonaphthalene-1-carboxylate (**11**).—A solution of 1,2,3,4-tetrahydro-1-methyl-4-oxonaphthalene-1-carboxylic acid[5] (**9**) (1 g, 4.9 mmol) in methanol (35 cm^3) containing conc. sulphuric acid (3 cm^3) and 20% oleum (0.4 cm^3) was heated under reflux (22 h). After evaporation of most of the methanol the cooled residue was added to ice (60 g) and extracted with ether (3 × 50 cm^3). The combined extracts were washed successively with very dil. (0.25M) aqueous sodium hydroxide (4 × 50 cm^3) and water (50 cm^3, 2 × 25 cm^3), and dried ($MgSO_4$). Evaporation gave the crude product (920 mg) which was purified by bulb-to-bulb distillation (0.4 mmHg; 125 °C) to give ester (**11**) as an oil (890 mg, 83%).

On a large scale the acid (33.4 g, 0.16 mol) was converted into the crude product (34.2 g) by reaction with methanol (1.2 l), conc. sulphuric acid (100 cm^3), and 20% oleum (13 cm^3) (22 h, reflux). Distillation under vacuum gave *ester* (**11**) (29.9 g, 85%)

as an oil, b.p. 118—119 °C/0.15 mmHg (Found: M^+, 218.0941. $C_{13}H_{14}O_3$ requires M, 218.0943); $\nu_{max.}$(film) 1 727s and 1 687s cm^{-1}; δ_H 8.05 (1 H, m, ArH), 7.65—7.25 (3 H, m, ArH), 3.67 (3 H, s), 2.70 (2 H, m), 2.58 (1 H, m), 2.10 (1 H, m), and 1.68 (3 H, s); *m/z* 218, 190, 160, 159, 147, and 131 (11, 42, 12, 100, 19, and 65%).

Methyl 8-Bromo-6,9-dihydro-5-methyl-9-oxo-5H-benzocycloheptene-5-carboxylate (**14**).—This was obtained by a three-step synthesis as follows.

(1) *The trimethylsilyl enol ether* (**12**).[2] To a stirred solution of ester (**11**) (19.8 g, 90.7 mmol) and triethylamine (36.7 g, 0.36 mol) in dry dimethylformamide (90 cm^3) under argon at room temperature was added chlorotrimethylsilane (19.7 g, 0.18 mol). The stirred mixture was heated under reflux (16 h), then cooled and added to ether (500 cm^3). After being washed with water (4 × 50 cm^3), the dried ($MgSO_4$) ether solution was evaporated to yield an orange oil (28.0 g) which was used in the subsequent experiment without further purification.

(2) *Addition to dibromocarbene.* A mixture of compound (**12**) (crude product from above, 28 g) and phenyl(tribromomethyl)mercury (40.0 g, 75.5 mmol) in dry 1,2-dimethoxyethane (180 cm^3) under argon was stirred and heated under reflux (110 min). The ice-cooled mixture was filtered, the residue was washed with ether (100 cm^3), and the combined filtrates were evaporated. The crude product (**13**) (a brown oil, 41.4 g) was used in the next step without further purification.

(3) *Ring-opening with* $AgBF_4$.[6] Silver tetrafluoroborate (16.2 g, 83.2 mmol) followed by methanol (100 cm^3) were added to a stirred solution of (**13**) (crude product from above, 41.4 g) in DME (100 cm^3) under argon. After being stirred and heated at reflux (50 min), the cooled mixture was filtered and the residue (a grey solid) was washed with ether (300 cm^3). The combined filtrate was washed with water (150 cm^3, 2 × 70 cm^3) and dried ($MgSO_4$). Evaporation gave the crude product (23.8 g) from which the title keto ester (**14**) was obtained by crystallisation (light petroleum–dichloromethane) [yield 7.6 g of (**14**), 27% based on (**11**), 33% based on $PhHgCBr_3$]. The crystallisation mother liquor residues were chromatographed on silica (210 g); elution with ether–benzene (1:19) gave a second crop of ester (**14**) [3.1 g, 11% based on (**11**), 13% based on $PhHgCBr_3$]. Continued elution with ether–benzene (1:19) gave starting material (**11**) (8.9 g, 45%). An analytical sample of keto ester (**14**) was crystallised as *white crystals* (light petroleum–dichloromethane) from chromatographed material, and had m.p. 126—126.5 °C (Found: C, 54.25; H, 4.15%; M^+, 308.0049 and 310.0028. $C_{14}H_{13}BrO_3$ requires C, 54.39; H, 4.24%; M, 308.0049[^{79}Br] and 310.0019 [^{81}Br]); $\nu_{max.}$ 1 727s and 1 649s cm^{-1}; $\lambda_{max.}$ 207 and 259 nm (ε 4 400 and 4 900 l mol^{-1} cm^{-1}); $\delta_H(CDCl_3)$ 7.8—7.2 (4 H, m, ArH), 7.29 (1 H, dd, *J* 7.5 and 3.5 Hz), 3.61 (3 H, s), 3.12 (1 H, dd, *J* 19 and 7.5 Hz), 2.53 (1 H, dd, *J* 19 and 3.5 Hz), and 1.76 (3 H, s). Irradiation of the peak at δ_H 7.29 causes both the signals at δ_H 3.12 and 2.53 to collapse to doublets; *m/z* 310 (M^+), 308 (M^+), 278, 276, 251, 249, 229, 197, 170, 169, 142, and 141 (15, 15, 22, 22, 34, 34, 38, 22, 82, 57, 94, and 100%).

Reaction of Keto Ester (**14**) *with* $NaBH_4$–$CeCl_3$.[7]—(1) *Small scale with separation of products.* To a stirred solution of keto ester (**14**) (350 mg, 1.1 mmol) and cerium(III) chloride heptahydrate (421 mg, 1.1 mmol) in methanol (25 cm^3) at room temperature was added sodium borohydride (43 mg, 1.1 mmol). After being stirred at room temperature (15 min) the solution was neutralised with dil. hydrochloric acid, and saturated brine (20 cm^3) was added. The methanol was removed by evaporation under reduced pressure and ether (50 cm^3) was added. The aqueous layer was extracted into ether (2 × 15 cm^3) and the combined ether phases were dried ($MgSO_4$) and evaporated. The crude product (315 mg) was chromatographed on silica (70 g); elution with ether–benzene (1:19) gave the *lactone* (**16**) (42 mg, 14%) as white prisms (from ether), m.p. 99—101 °C (Found: C, 55.8; H, 4.0%; M^+, 277.9943 and 279.9920. $C_{13}H_{11}BrO_2$ requires C, 55.94; H, 3.97%; M, 277.9943 and 279.9923); $\nu_{max.}$ 1 751s cm^{-1}; $\delta_H(CDCl_3)$ 7.6—7.1 (4 H, m, ArH), 5.86 (1 H, td, *J* 4 and 1.5 Hz), 5.56 (1 H, d, *J* 1.5 Hz), 2.70 (1 H, dd, *J* 19 and 4 Hz), 2.22 (1 H, dd, *J* 19 and 4 Hz), and 1.72 (3 H, s); *m/z* 280 (M^+), 278 (M^+), 236, 234, 221, 219, 171, and 155 (8, 8, 15, 15, 21, 21, 13, and 100%).

Continued elution with ether–benzene (1:19) gave starting material (**14**) (54 mg, 15%). Continued elution with the same solvent system then gave the *alcohol* (**15**) as an oil (175 mg, 51%) (one isomer by n.m.r. spectroscopy) (Found: M^+, 310.0205 and 312.0185. $C_{14}H_{15}BrO_3$ requires M, 310.0205 [^{79}Br] and 312.0185 [^{81}Br]); $\nu_{max.}$(film) 3 480br s and 1 730s cm^{-1}; $\delta_H(CDCl_3)$ 7.8—7.5 (1 H, m, ArH), 7.4—7.1 (3 H, m, ArH), 6.17 (1 H, td, *J* 6 and 2 Hz), 5.69 (1 H, br d, *J* 5.5 Hz), 3.67 (3 H, s), 3.16 (1 H, ddd, *J* 16, 6, and 2 Hz), 2.65 (1 H, d, *J* 5.5 Hz, OH), 2.29 (1 H, ddd, *J* 16, 6, and 2 Hz), and 1.61 (3 H, s); on addition of D_2O the signal at δ_H 5.69 collapsed to a broadened singlet; *m/z* 312 (M^+), 310 (M^+), 235, 233, 231, 213, 199, and 171 (9, 9, 21, 18, 33, 18, 52, and 100%).

(2) *Large scale without separation of individual products.* Sodium borohydride (1.96 g, 51.8 mmol) was added to a stirred solution of keto ester (**14**) (10.7 g, 34.6 mmol) and cerium(III) chloride heptahydrate (19.3 g, 51.8 mmol) in methanol (650 cm^3) at room temperature. The solution was stirred at room temperature (70 min), then made neutral with dil. hydrochloric acid. After the addition of conc. brine (200 cm^3) and removal of methanol by evaporation under reduced pressure, the residue was extracted into ether (100 cm^3, 3 × 70 cm^3). The combined extracts were washed with water (20 cm^3), dried ($MgSO_4$), and evaporated. Passage of the crude product (9.55 g) through a short column of silica (65 g) in ether–benzene (1:19) gave a product (9.25 g) which, by n.m.r. spectroscopy, consisted of a mixture of compounds (**15**) and (**16**) [*ca.* 3:1 from n.m.r. integrals; starting material (**14**) absent]. This mixture was converted directly into bromo ester (**17**) with MeOH–HCl (see below).

Methyl 8-Bromo-5-methyl-5H-benzocycloheptene-5-carboxylate (**17**).—(*a*) A solution of of compound (**15**) (105 mg, 0.34 mmol) in methanol (6 cm^3) saturated with dry hydrogen chloride was heated under reflux ($CaCl_2$ drying tube), (12 h). The solution was periodically resaturated with hydrogen chloride during the heating period. The cooled solution was added to water (5 cm^3) and extracted into ether (4 × 8 cm^3). The combined extracts were washed with water (4 cm^3), dried ($MgSO_4$) and evaporated to give the crude product (85 mg). Chromatography on silica (50 g) in ether–light petroleum (1:4) as eluant gave the *title compound* (**17**) (65 mg, 65%) as white prisms (from light petroleum–dichloromethane), m.p. 88.5—89 °C (Found: C, 57.15; H, 4.35%; M^+, 292.0099 and 294.0082. $C_{14}H_{13}BrO_2$ requires C, 57.36; H, 4.47%; M, 292.0099 [^{79}Br] and 294.0079 [^{81}Br]), $\nu_{max.}$(CCl_4) 1 740s cm^{-1}; $\lambda_{max.}$(EtOH) 204, 236sh, and 275 nm (ε 20 400, 7 900, and 8 200); $\delta_H(CDCl_3)$ 7.7—7.15 (4 H, m, ArH), 7.48 (1 H, s [slightly broadened]), 6.23 (1 H, d, [wffs], *J* 10 Hz), 5.57 (1 H, d, *J* 10 Hz), 3.52 (3 H, s), and 1.88 (3 H, s); *m/z* 294 (M^+), 292 (M^+), 235, 233, 213, and 153 (8, 8, 52, 57, 53, and 100%).

(*b*) A solution of lactone (**16**) (38 mg, 0.14 mmol) in methanol (4 cm^3) was heated at reflux ($CaCl_2$ drying tube) while dry hydrogen chloride was passed into it continuously (6.5 h). Water (6 cm^3) was added and the solution was extracted into ether (3 × 7 cm^3). The combined extracts were washed successively with dil. aqueous sodium hydrogen carbonate (2 × 4 cm^3) and saturated brine (4 cm^3). After the extracts had been dried ($MgSO_4$), evaporation gave the crude product (33

mg) which was chromatographed on silica (22 g); elution with ether–light petroleum (1:4) gave the title compound (**17**) (26 mg, 64%), identical (t.l.c., m.p., n.m.r., i.r.) with that described above.

(*c*) Dry hydrogen chloride was passed continuously through a solution of the previously prepared mixture (9.25 g) of compounds (**15**) and (**16**) in methanol (200 cm^3) which was heated at reflux ($CaCl_2$ drying tube; 8.5 h). The cooled mixture was added to ice (150 g) and extracted into ether (120 cm^3, 3 × 80 cm^3). The combined extracts were washed successively with dil. aqueous sodium hydrogen carbonate (3 × 25 cm^3) and saturated brine (2 × 25 cm^3), then dried ($MgSO_4$) and evaporated. Chromatography of the crude product (8.2 g) on silica (220 g) in ether–light petroleum (1:4) gave the title compound (**17**) [5.9 g, 58% based on the ketone (**14**)], identical (t.l.c., n.m.r.) with that described above.

(8-*Bromo*-5-*methyl*-5H-*benzocyclohepten*-5-*yl*)*methanol* (**18**).—Di-isobutylaluminium hydride (50 mmol) in hexane (1M; 50 cm^3) was added by syringe to a stirred solution of ester (**17**) (5.4 g, 18.4 mmol) in dry toluene (70 cm^3) under argon at −65 °C. After the mixture had been stirred while its temperature rose to −15 °C (110 min), methanol (15 cm^3) was added to the cooled (−40 °C) solution and the mixture was stirred and allowed to attain room temperature (10 min). Water (30 cm^3) and ether (90 cm^3) were added and after being stirred for 15 min, the mixture was filtered and the residue triturated with ether (3 × 50 cm^3). The combined ether solution was washed successively with dil. hydrochloric acid (2 × 30 cm^3), dil. aqueous sodium hydrogen carbonate (2 × 30 cm^3), and saturated brine (2 × 30 cm^3), and was then dried ($MgSO_4$) and evaporated. Chromatography of the crude product (5.2 g) on silica (130 g) in benzene–dichloromethane (1:4) gave, first, starting material (**17**) (560 mg, 10%), then the *title compound* (**18**) (4.1 g, 84%) as a pale yellow oil (Found: M^+, 264.0150 and 266.0127. $C_{13}H_{13}BrO$ requires 264.0150 [^{79}Br] and 266.0131 [^{81}Br]); $\nu_{max.}$ (neat film) 3 380br m cm^{-1}; $\lambda_{max.}$(EtOH) 205 and 288 nm (ε 17 200 and 7 850); δ_H($CDCl_3$) 7.6—7.1 (5 H, m, 4 ArH and 1 olefinic H), 6.24 (1 H, dd, *J* 11 and 1.5 Hz), 5.36 (1 H, d, *J* 11 Hz), 3.65 (1 H, d, *J* 10 Hz), 3.50 (1 H, d, *J* 10 Hz), 1.60 (1 H, s, OH), and 1.53 (3 H, s); *m*/*z* 266 (M^+), 264 (M^+), 235, 233, and 153 (6, 6, 98, 100, and 69%).

8-*Bromo*-5-*methyl*-5H-*benzocycloheptene*-5-*carbaldehyde* (**19**).—Chromium trioxide (3.34 g, 33.4 mmol) was added to a stirred solution of dry pyridine (5.3 g, 67 mmol) in dry dichloromethane (110 cm^3) under argon at room temperature, and the resulting solution was stirred for 40 min. A solution of the alcohol (**18**) (985 mg, 3.71 mmol) in dichloromethane (20 cm^3) was added and caused immediate separation of a black tar. After the mixture had been stirred at room temperature for 45 min, ether (150 cm^3) was added and the solution was washed successively with dil. aqueous sodium carbonate (5 × 30 cm^3), dil. hydrochloric acid (5 × 30 cm^3), dil. aqueous sodium hydrogen carbonate (2 × 30 cm^3) and saturated brine (2 × 30 cm^3), and was then dried ($MgSO_4$). Evaporation gave the crude product (930 mg) which was chromatographed on silica (125 g); elution with benzene gave the *title compound* (**19**) (877 mg, 90%) as fine white needles (from light petroleum–dichloromethane), m.p. 47—48 °C (Found: C, 59.25; H, 4.25%; M^+, 261.9991 and 263.9975. $C_{13}H_{11}BrO$ requires C, 59.34; H, 4.21%; *M*, 261.9994 [^{79}Br] and 263.9974 [^{81}Br]; $\nu_{max.}$(CCl_4) 1 735s cm^{-1}; $\lambda_{max.}$(EtOH) 204 and 282 nm (ε 18 500 and 7 550); δ_H($CDCl_3$) 9.16 (1 H, s), 7.46 (1 H, br s, olefinic), 7.65—7.10 (4 H, m, ArH), 6.41 (1 H, dd, *J* 10 and 1.0 Hz), 5.49 (1 H, d, *J* 10 Hz), and 1.67 (3 H, s); *m*/*z* 264 (M^+), 262 (M^+), 235, 233, 183, and 153 (4, 4, 99, 100, 15, and 64%).

(5-*Methyl*-5H-*benzocyclohepten*-5-*yl*)*methanol* (**28**).—n-Butyl-lithium in hexane (1.35M; 0.2 cm^3, 0.27 mmol) was syringed into a stirred solution of the bromo alcohol (**18**) (28 mg, 0.106 mmol) in dry ether (0.5 cm^3) under argon at −50 °C. After being stirred at −50 °C for 30 min, the solution was allowed to warm up to −20 °C and was stirred for 60 min. Water (1 cm^3) and ether (10 cm^3) were added and the organic layer was washed successively with saturated aqueous ammonium chloride (2 × 2 cm^3) and water (2 cm^3), and was then dried ($MgSO_4$) and evaporated. The residue (20 mg) was chromatographed on silica (10 g); elution with ether–benzene (1:9) gave the *title compound* (**28**) (19 mg, 96%) as an oil (Found: M^+, 186.1042. $C_{13}H_{14}O$ requires *M*, 186.1045); $\nu_{max.}$ (neat film) 3 385br s cm^{-1}; $\lambda_{max.}$(EtOH) 206 and 285 nm (ε 16 100 and 6 700); δ_H($CDCl_3$) 7.55—7.10 (4 H, m, ArH), 7.03 (1 H, d, [wffs], *J* 11 Hz), 6.38 (1 H, ddd, *J* 11, 6, and 1 Hz), 6.18 (1 H, ddd, *J* 10, 6, and 1 Hz), 5.42 (1 H, dd, *J* 10 and 1 Hz), 3.55 (2 H, br m), 1.63 (3 H, s), and 1.03 (1 H, br s, OH); on addition of D_2O the signal at δ_H 3.55 was resolved into doublets, δ_H 3.62 (1 H, d, *J* 11 Hz), and 3.47 (1 H, d, *J* 11 Hz); *m*/*z* 186, 168, and 155 (3, 7, and 100%).

On a large scale compound (**18**) (4.1 g, 15.5 mmol) in ether (50 cm^3) at −50 °C was converted into product (**28**) with n-butyl-lithium in hexane (1.35M; 29 cm^3, 39 mmol) (at −50 °C for 20 min, then at −20 °C for 60 min). Addition of saturated aqueous ammonium chloride (15 cm^3) followed by work-up as described above gave the crude product (2.8 g) which was shown to be very pure compound (**28**) by n.m.r. spectroscopy and t.l.c. This product was oxidised to the aldehyde (**29**) without further purification as described below.

5-*Methyl*-5H-*benzocycloheptene*-5-*carbaldehyde* (**29**).—(*a*) Chromium trioxide (970 mg, 9.7 mmol) was added to a stirred solution of dry pyridine (1.52 g, 19.2 mmol) in dry dichloromethane (30 cm^3) at room temperature under argon. After the mixture had been stirred for a further 40 min, a solution of the alcohol (**28**) (200 mg, 1.07 mmol) in dichloromethane (5 cm^3) was added and the resulting solution, from which a black tar immediately separated, was stirred at 20 °C for 55 min. The product was diluted with ether (70 cm^3) and washed successively with dil. aqueous carbonate (4 × 30 cm^3), dil. hydrochloric acid (4 × 20 cm^3), dil. aqueous sodium hydrogen carbonate (2 × 30 cm^3), and water (2 × 30 cm^3). The solution was dried ($MgSO_4$) and evaporated to give the crude product (162 mg) which was purified by chromatography on silica (40 g); elution with benzene gave the *title compound* (**29**) as an oil (124 mg, 63%) (Found, M^+, 184.0886. $C_{13}H_{12}O$ requires *M*, 184.0888); $\nu_{max.}$ (neat film) 1 729s cm^{-1}; $\lambda_{max.}$(EtOH) 204 and 276 nm (ε 20 200 and 7 200); δ_H($CDCl_3$) 9.07 (1 H, s), 7.70—7.10 (4 H, m, ArH), 7.04 (1 H, d, *J* 12 Hz), 6.33 (2 H, two superimposed m), 5.52 (1 H, d, *J* 10 Hz), and 1.65 (3 H, s); *m*/*z* 184, 156, and 155 (11, 13, and 100%).

(*b*) A solution of dimethyl sulphoxide (2.42 g, 31 mmol) in dichloromethane (8 cm^3) was added to a stirred solution of oxalyl chloride (1.89 g, 14.9 mmol) in dry dichloromethane (30 cm^3) under argon at −55 °C. After being stirred for a further 3 min, the mixture was treated with a solution of the alcohol (**28**) (2.45 g, 13.15 mmol) in dichloromethane (10 cm^3), and this mixture was stirred at −55 °C for another 20 min. Triethylamine (6.7 g, 66 mmol) was added and, after being stirred at −55 °C for 5 min, the solution was allowed to attain room temperature, and then water (60 cm^3) was added. The product was extracted into ether (3 × 50 cm^3) and the combined extracts were washed with saturated brine (3 × 15 cm^3), dried ($MgSO_4$), and evaporated. The crude product (2.4 g) was chromatographed on silica (130 g); elution with benzene gave the aldehyde (**29**) as an oil (2.2 g, 90%), identical (n.m.r., t.l.c.) with that described above.

4-Cyano-4-phenylpentanoic Acid (**8**).—A solution of methyl 4-cyano-4-phenylpentanoate[5] (3 g, 13.8 mmol) and sodium carbonate decahydrate (15.8 g, 55.2 mmol) in a mixture of water (90 cm^3) and ethanol (40 cm^3) was stirred at 20 °C for 70 h. Water (100 cm^3) was added and the solution was extracted with dichloromethane (2 × 25 cm^3). The aqueous layer was made acidic with conc. hydrochloric acid, the acidic product was extracted into dichloromethane (4 × 50 cm^3), and the extract was washed with water (20 cm^3), dried ($MgSO_4$), and evaporated to give the crude acid (**8**). The reaction was repeated on the same scale (3 g) and the combined crude product (3 g) was chromatographed on silica (210 g); elution with benzene–acetic acid (93:7) gave the *title compound* (**8**) (3.4 g, 61%) as fine white needles (from benzene–light petroleum), m.p. 75—76 °C (Found: C, 71.05; H, 6.7; N, 7.0%; M^+, 203.0949. $C_{12}H_{13}NO_2$ requires C, 70.9; H, 6.45; N, 6.9% *M*, 203.0946); $\nu_{max.}(CCl_4)$ 2 986br m, 2 237w, and 1 715s cm^{-1}; $\delta_H(CDCl_3)$ 9.20 (1 H, br s, CO_2H), 7.50—7.15 (5 H, m, Ph), 2.75—2.05 (4 H, overlapping m), and 1.75 (3 H, s); *m/z* 203, 130, and 103 (13, 100, and 26%).

1,2,3,4-Tetrahydro-1-methyl-4-oxonaphthalene-1-carbonitrile (**10**).—A solution of the acid (**8**) (2.8 g, 13.8 mmol) in oxalyl chloride (21.8 g, 0.17 mmol) was stirred at 20 °C for 3 h. Evaporation of the oxalyl chloride followed by addition and evaporation of dry benzene (3 × 15 cm^3) gave the acid chloride (3.05 g) as a yellow oil which was used in the next step without further purification; $\nu_{max.}$ (neat film) 2 240w and 1 800s cm^{-1}.

The foregoing acid chloride (3.05 g) and anhydrous aluminium chloride (3.67 g, 27.5 mmol) were heated in dry carbon disulphide (40 cm^3) under reflux (40 min; $CaCl_2$ drying tube). The cooled mixture was added to a mixture of dil. hydrochloric acid (100 cm^3) and ice (30 g) and extracted into ether (4 × 40 cm^3). The combined extract was washed successively with dil. aqueous sodium hydrogen carbonate (3 × 25 cm^3) and water (2 × 25 cm^3), and was then dried ($MgSO_4$) and evaporated. Chromatography of the crude product (1.87 g) on silica (50 g) in benzene–chloroform (1:1) as eluant gave the *tetralone* (**10**) [1.52 g, 59% based on the acid (**8**)] as white prisms (from dichloromethane–light petroleum), m.p. 56—57 °C (Found: C, 77.85; H, 6.0; N, 7.5%; M^+, 185.0841. $C_{12}H_{11}NO$ requires C, 77.8; H, 6.0; N, 7.6%; *M*, 185.0841); $\nu_{max.}$ 2 230w and 1 678s cm^{-1}; $\delta_H(CDCl_3)$ 8.08 (1 H, m, ArH), 7.80—7.25 (3 H, m, ArH), 2.87 (2 H, m), 2.53 (1 H, m), 2.38 (1 H, m), and 1.82 (3 H, s); *m/z* 185, 157, and 129 (43, 100, and 30%).

6-Bromo-9-cyano-8,9-dihydro-9-methyl-5H-benzocyclohepten-5-one (**36**).—To a stirred solution of the tetralone (**10**) (1.2 g, 6.48 mmol) and triethylamine (2.61 g, 25.8 mmol) in dry DMF (7 cm^3) at 20 °C under argon was added chlorotrimethylsilane (1.41 g, 13.0 mmol). The mixture was heated at reflux (16 h), then cooled and added to ether (70 cm^3); the mixture was washed with water (20 cm^3, 4 × 10 cm^3) and dried ($MgSO_4$). Evaporation gave the product (1.89 g) which was mixed with phenyl(tribromomethyl)mercury (3.77 g, 7.12 mmol) in dry DME (15 cm^3) and the mixture was heated at reflux under argon for 2 h. The ice-cooled product was filtered, the residue was washed with ether (40 cm^3), and the combined filtrate was evaporated. A solution of the crude product (3.1 g) in DME (10 cm^3) was added to a solution of silver tetrafluoroborate (1.39 g, 7.1 mmol) in dry methanol (10 cm^3) and the mixture was heated at reflux under argon (45 min). The ice-cooled mixture was filtered and the residue was washed with ether (50 cm^3). The combined filtrate was washed with water (3 × 10 cm^3), dried ($MgSO_4$), and evaporated. The crude product (1.56 g) was chromatographed on silica (220 g); elution with ether–benzene (3:97) gave the *title compound* (**36**) [670 mg, 37% based on the ketone (**10**)] as white prisms (from dichloromethane–light petroleum), m.p. 134—135 °C (Found: C, 56.4; H, 3.55; N, 4.95%; M^+, 274.9949 and 276.9925. $C_{13}H_{10}BrNO$ requires C, 56.55; H, 3.65; N, 5.1%; *M*, 274.9946 [^{79}Br] and 276.9927 [^{81}Br]); $\nu_{max.}$ 2 225w and 1 657s cm^{-1}; $\lambda_{max.}$ 209 and 260 nm (ε 6 100 and 5 550); δ_H 7.85—7.35 (4 H, m, ArH), 7.21 (1 H, dd, *J* 6 and 5 Hz), 3.14 (1 H, dd, *J* 19 and 5 Hz), 2.88 (1 H, dd, *J* 19 and 6 Hz), and 1.84 (3 H, s); *m/z* 277 (M^+), 275 (M^+), 196, 168, 153, 141, and 129 (22, 22, 73, 38, 52, 44, and 100%). Continued elution with the same solvent system gave starting material (**10**) (40 mg, 3%).

Reduction of Ketone (**36**) *with* $NaBH_4$–$CeCl_3$.—Sodium borohydride (99 mg, 2.26 mmol) was added to a stirred solution of ketone (**36**) (600 mg, 2.17 mmol) and cerium(III) chloride heptahydrate (970 mg, 2.60 mmol) in methanol (40 cm^3) at 20 °C. After being stirred at 20 °C for 30 min the solution was neutralised with dil. hydrochloric acid, and conc. brine (25 cm^3) was added. After removal of methanol by evaporation under reduced pressure (40 °C) the product was extracted into ether (30 cm^3, 4 × 15 cm^3), the extract was dried ($MgSO_4$). Evaporation gave the crude product (500 mg) which was chromatographed on silica (120 g); elution with ether–benzene (4:96) gave, first, the lactone (**16**) (90 mg, 15%), identical (t.l.c., n.m.r., i.r.) with that described above. Continued elution with ether–benzene (4:96) gave the *cyano alcohol* (**37**) (365 mg, 60%) as white prisms (from acetone–light petroleum), m.p. 111—112 °C (Found: C, 56.05; H, 4.35; N, 5.1%; M^+, 277.0105 and 279.0091. $C_{13}H_{12}BrNO$ requires C, 56.1; H, 4.35; N, 5.0%; *M*, 277.0103 [^{79}Br] and 279.0083 [^{81}Br]); $\nu_{max.}$ 3 455s and 2 245w cm^{-1}; δ_H 7.75—7.20 (4 H, m, ArH), 6.23 (1 H, ddd, *J* 6, 5.5, and 1 Hz), 5.78 (1 H, br d, *J* 4.5 Hz), 2.97 (1 H, ddd, *J* 17, 5.5, and 1.7 Hz), 2.73 (1 H, ddd, *J* 17, 6, and 1.6 Hz), 2.64 (1 H, d, *J* 4.5 Hz, OH), and 1.92 (3 H, s); on addition of D_2O the signal at δ_H 5.78 collapsed to a broadened singlet; *m/z* 279 (M^+), 277 (M^+), 198, 171, 159, 153, 143, and 128 (3, 3, 36, 47, 20, 21, 100, and 45%).

8-Bromo-5-methyl-5H-benzocycloheptene-5-carbonitrile (**21**).—A solution of the alcohol (**37**) (285 mg, 1.02 mmol), carbon tetrabromide (677 mg, 2.04 mmol), and triphenylphosphine (321 mg, 1.22 mmol) in dry acetonitrile (9 cm^3) was heated at reflux under argon for 135 min. After evaporation of solvent, the residue was triturated with ether (4 × 10 cm^3) and the combined ether solution was evaporated. By n.m.r. spectroscopy and t.l.c. the crude product (715 mg) was shown to contain the required nitrile (**21**) and two dibromo compounds.

A solution of the crude product and DBU (311 mg, 2.04 mmol) in dry benzene (12 cm^3) was heated at reflux under argon for 45 min, and was then added to ether (30 cm^3) and the mixture was washed successively with dil. hydrochloric acid (8 × 5 cm^3), dil. aqueous sodium hydrogen carbonate (2 × 5 cm^3), and water (2 × 5 cm^3), dried ($MgSO_4$), and evaporated to give the crude product (370 mg) which was chromatographed on silica (75 g); elution with ether–light petroleum (1:4) gave the *title compound* (**21**) (110 mg, 41%) as white prisms (from light petroleum–dichloromethane), m.p. 100—101 °C (Found: C, 59.7; H, 3.85; N, 5.2%; M^+, 258.9996 and 260.9977. $C_{13}H_{10}BrN$ requires C, 60.0; H, 3.90; N, 5.4%; *M*, 258.9997 [^{79}Br] and 260.9977 [^{81}Br]; $\nu_{max.}(CCl_4)$ 2 337s cm^{-1}; $\lambda_{max.}$ 203, 228sh, and 282 nm (ε 20 000, 6 400, and 7 100); δ_H 7.66 (1 H, br s, olefinic), 7.70—7.20 (4 H, m, ArH), 6.31 (1 H, dd, *J* 10 and 0.8 Hz), 5.53 (1 H, d, *J* 10 Hz), and 1.91 (3 H, s); *m/z* 261 (M^+), 259 (M^+), 246, 244, 180, and 153 (3, 3, 7, 7, 100, and 38%).

5-Methyl-5H-benzocycloheptene-5-carbaldehyde Oxime.—A solution of the aldehyde (**29**) (200 mg, 1.09 mmol) in chloroform (0.4 cm^3) was added to a solution of hydroxylamine hydrochloride (417 mg, 6.00 mmol) in ethanol (3 cm^3) containing water (0.5 cm^3). Pyridine (489 mg, 6.18 mmol) was added and the solution was stirred at 20 °C for 80 min. The product was

added to ether (20 cm^3) and washed successively with dil. hydrochloric acid (3 × 2 cm^3), dil. aqueous sodium hydrogen carbonate (2 × 2 cm^3), and saturated brine (2 × 2 cm^3), and the solution was then dried ($MgSO_4$). Evaporation gave a white solid (215 mg) from which the *title compound* (180 mg, 83%) (one isomer) was crystallised (from light petroleum–dichloromethane) as fine white needles, m.p. 139—141 °C (Found: C, 78.1; H, 6.5; N, 7.15%; M^+, 199.0999. $C_{13}H_{13}NO$ requires C, 78.4; H, 6.6; N, 7.0%; *M*, 199.0997); $\nu_{max.}$(CCl_4) 3 598sharp s and 3 315br m cm^{-1}; $\lambda_{max.}$ 205 and 279 nm (ε 21 000 and 6 600); δ_H 7.45 (1 H, s, OH), 7.57—7.15 (4 H, m, ArH), 7.16 (1 H, s, CH=N), 7.11 (1 H, br d, *J* 10 Hz), 6.42 (1 H, ddd, *J* 10, 5.5, and 0.8 Hz), 6.19 (1 H, ddd, *J* 10, 5.5, and 0.9 Hz), 5.58 (1 H, br d, *J* 10 Hz), and 1.73 (3 H, s); *m/z* 199, 182, 167, and 153 (12, 90, 100, and 69%).

The crystallisation mother liquor residues (35 mg) consisted of both the *syn* and *anti* isomers of the oxime (n.m.r. spectrum).

5-Methyl-5H-benzocycloheptene-5-carbonitrile (**34**).—A solution of the foregoing oxime (240 mg, 1.20 mmol) in acetic anhydride (5 cm^3) was heated under reflux (30 min; $CaCl_2$ drying tube). Evaporation of the solvent under reduced pressure on a steam-bath gave the crude product (310 mg) which was chromatographed on silica (75 g); elution with benzene–light petroleum (6:4) gave the *title compound* (**34**) (55 mg, 25%) as white prisms (from light petroleum–dichloromethane); m.p. 39—41 °C (Found: C, 86.15; H, 6.2; N, 7.65%; M^+, 181.0890. $C_{13}H_{11}N$ requires C, 86.15; H, 6.1; N, 7.7%; *M*, 181.0891); $\nu_{max.}$(CCl_4) 2 215w cm^{-1}; $\lambda_{max.}$ 205 and 274 nm (ε 19 350 and 7 900); δ_H 7.70—7.20 (4 H, m, ArH), 7.27 (1 H, d, *J* 11 Hz), 6.59 (1 H, dd, *J* 12 and 6 Hz), 6.19 (1 H, dd, *J* 11 and 6 Hz), 5.55 (1 H, d, *J* 12 Hz), and 1.91 (3 H, s); *m/z* 181, 166, 153, 140, and 128 (42, 100, 19, 21, and 17%).

8-Bromo-5-(2′,2′-dibromovinyl)-5-methyl-5H-benzocycloheptene.—Triphenylphosphine (1.84 g, 7.02 mmol) was added to a stirred solution of carbon tetrabromide (1.30 g, 3.92 mmol) in dry dichloromethane (8 cm^3) under argon at 20 °C. After the mixture had been stirred for a further 15 min, a solution of the bromo aldehyde (**19**) (205 mg, 0.78 mmol) in dichloromethane (4 cm^3) was added and the mixture was stirred for another 90 min. After addition of light petroleum (50 cm^3), the cooled 0 °C mixture was filtered. Evaporation of the filtrate gave a residue (710 mg) which was chromatographed on silica (75 g); elution with benzene–light petroleum (1:19) gave the *title compound* (305 mg, 93%) as an oil (Found: M^+, 417.8393 and 419.8367. $C_{14}H_{11}Br_3$ requires *M*, 417.8393 [$^{79}Br_2{}^{81}Br$] and 419.8373 [$^{79}Br^{81}Br_2$]); $\nu_{max.}$ (neat film) 1 612m, 1 596m, 1 485m, 1 481m, 1 373m, 1 016m, 880m, 870m, 825s, 799m, 754s, and 736s cm^{-1}; $\lambda_{max.}$ 205 and 283 nm (ε 25 350 and 8 100); δ_H 7.57 (1 H, br s), 7.75—7.15 (4 H, m, ArH), 6.22 (1 H, s, CH=CBr_2), 6.15 (1 H, d [wffs], *J* 10 Hz), 5.55 (1 H, d, *J* 10 Hz), and 1.86 (3 H, s); *m/z* 420 (M^+), 418 (M^+), 341, 339, 337, 260, 259, 258, 257, and 179 (0.3, 0.3, 6, 13, 7, 23, 27, 26, 24, and 100%).

5-(2′,2′-Dibromovinyl)-5-methyl-5H-benzocycloheptene (**30**).—Triphenylphosphine (1.42 g, 5.41 mmol) was added to a stirred solution of carbon tetrabromide (995 mg, 3.00 mmol) in dry dichloromethane (4 cm^3) at 20 °C. After the mixture had been stirred for another 15 min, a solution of the aldehyde (110 mg, 0.60 mmol) in dichloromethane (1 cm^3) was added and the mixture was stirred for a further 100 min. After addition of light petroleum (25 cm^3), the cooled (0 °C) mixture was filtered and the filtrate was evaporated to give the crude product (470 mg). Chromatography on silica (75 g) in benzene–light petroleum (1:19) as eluant gave the *title compound* (**30**) (171 mg, 84%) as white prisms (from methanol–dichloromethane), m.p. 46—47 °C (Found: C, 49.4; H, 3.45%; M^+, 337.9309, 339.9292, and 341.9272. $C_{14}H_{12}Br_2$ requires C, 49.45; H, 3.6%; *M*, 337.9307 [$^{79}Br_2$], 339.9287 [$^{81}Br^{79}Br$], and 341.9267 [$^{81}Br_2$]); $\nu_{max.}$(CCl_4) 3 030s, 1 598m, 1 483m, 1 461s, 1 367s, 1 042s, 709s, and 697s cm^{-1}; $\lambda_{max.}$ 205 and 276 nm (ε 26 500 and 6 600); δ_H 7.70—7.10 (4 H, m, ArH), 7.16 (1 H, d, *J* 12 Hz), 6.46 (1 H, dd, *J* 12 and 5 Hz), 6.18 (1 H, s, CH=CBr_2), 6.07 (1 H, dd, *J* 10 and 5 Hz), 5.61 (1 H, d, *J* 10 Hz), and 1.85 (3 H, s); *m/z* 342 (M^+), 340 (M^+), 338 (M^+), 261, 259, 180, and 179 (0.9, 1.9, 0.9, 8, 8, 84, and 100%).

5-Ethynyl-5-methyl-5H-benzocycloheptene (**23**) *and* *5-Ethynyl-9-methyl-5H-benzocycloheptene* (**24**).—To a stirred solution of 8-bromo-5-(2′,2′-dibromovinyl)-5-methyl-5*H*-benzocycloheptene (234 mg, 0.56 mmol) in dry ether (2 cm^3) under argon at −65 °C was added n-butyl-lithium in hexane (1.35M; 1.9 cm^3, 2.57 mmol). The dark green solution was stirred at −65 °C (30 min) then at −15 °C (1 h), and quenched with saturated aqueous ammonium chloride (4 cm^3). Ether (10 cm^3) was added and the organic layer was washed successively with saturated aqueous ammonium chloride (3 cm^3) and saturated brine (2 × 3 cm^3), dried ($MgSO_4$), and evaporated. Chromatography of the crude product (90 mg) on silica (55 g) in dichloromethane–light petroleum (1:19) as eluant gave, first, the rearranged *acetylene* (**24**) (8 mg, 8%) as an oil (Found: M^+, 180.0932. $C_{14}H_{12}$ requires *M*, 180.0939); $\nu_{max.}$ (neat film) 3 300s and 2 125w cm^{-1}; $\lambda_{max.}$ 203 and 266 nm (ε 13 400 and 3 900); δ_H 7.95—7.15 (4 H, m, ArH), 6.44 (1 H, d, [wffs], *J* 5 Hz), 5.96 (1 H, dd [wffs], *J* 9 and 5 Hz), 5.67 (1 H, dd [wffs], *J* 9 and 5.5 Hz), 3.55 (1 H, d [wffs], *J* 5.5 Hz), 2.43 (1 H, d, *J* 2.5 Hz, C≡CH), and 2.39 (3 H, br s, Me); *m/z* 180, 165, 152, and 115 (35, 100, 9, and 9%).

Continued elution with dichloromethane–light petroleum (1:19) gave a mixed fraction of isomers (**23**) and (**24**) (15 mg, 15%), followed by pure unrearranged *acetylene* (**23**) (55 mg, 54%) as an oil (Found: M^+, 180.0941); $\nu_{max.}$ (neat film) 3 295s and 2 112w cm^{-1}; $\lambda_{max.}$ 203 and 279 nm (ε 19 400 and 7 350); δ_H 7.79 (1 H, m, ArH), 7.60—7.20 (3 H, m, ArH), 7.11 (1 H, d, *J* 11 Hz), 6.43 (1 H, dd [wffs], *J* 11 and 6 Hz), 6.08 (1 H, dd [wffs], *J*, 10 and 6 Hz), 5.79 (1 H, d [wffs], *J* 10 Hz), 2.33 (1 H, s, C≡CH), and 1.57 (3 H, s); *m/z* 180, 165, 152, 139, 128, and 115 (34, 100, 8, 8, 7, and 11%).

The same two acetylenes were obtained from 5-(2′,2′-dibromovinyl)-5-methyl-5*H*-benzocycloheptene (**30**) upon similar reaction with Bu^nLi.

(5-Methyl-5H-benzocyclohepten-5-yl)ethynyl Phenyl Ketone (**31**).—Bis(triphenylphosphine)palladium dichloride (1 mg) and copper(I) iodide (1 mg) were added to a stirred solution of compound (**23**) (50 mg, 0.28 mmol) and benzoyl chloride (40 mg, 0.28 mmol) in triethylamine (0.5 cm^3) under argon at 20 °C. The mixture was stirred at 20 °C for 17 h, methanol (2 cm^3) was added, and all solvent was removed by evaporation under reduced pressure (30 °C). The residue was added to benzene (10 cm^3) and washed with dil. hydrochloric acid (2 cm^3), dil. aqueous sodium hydrogen carbonate (2 × 1 cm^3), and water (2 × 1 cm^3). After drying ($MgSO_4$), and evaporation of solvent, the crude product (80 mg) was chromatographed on silica (35 g); elution with ether–light petroleum (1:19) gave the *title compound* (**31**) (56 mg, 70%) as a pale yellow oil (Found: M^+, 284.1203. $C_{21}H_{16}O$ requires *M*, 284.1201); $\nu_{max.}$ (neat film) 2 205s and 1 643s cm^{-1}; $\lambda_{max.}$ 202 and 262 nm (ε 28 100 and 17 400); δ_H 8.05 (2 H, m, ArH), 7.75—7.15 (7 H, m, ArH), 7.22 (1 H, d [wffs], *J* 11 Hz), 6.54 (1 H, dd [wffs], *J* 11 and 5.5 Hz), 6.19 (1 H, dd [wffs], *J* 10 and 5.5 Hz), 5.76 (1 H, d [wffs], *J* 10 Hz), and 1.88 (3 H, s); *m/z* 284, 269, 241, 239, 179, and 105 (56, 8, 17, 12, 30, and 100%).

Attempted Rearrangement of Compound (**23**) *with n-Butyl-*

lithium.—To a stirred solution of the acetylene (**23**) (7 mg, 0.04 mmol) in dry ether (0.5 cm^3) under argon at −78 °C was added n-butyl-lithium in hexane (1.35M; 0.06 cm^3, 0.08 mmol). The solution was allowed to attain a temperature of −20 °C, and was then stirred for 20 h and quenched with saturated aqueous ammonium chloride (1 cm^3). Addition of ether (5 cm^3) and work-up in the usual way gave the crude product (7 mg) which was shown (n.m.r, t.l.c.) to contain only starting material (**23**); the rearranged acetylene (**24**) was absent.

8-*Bromo-5-methyl-*5H-*benzocyclohepten-5-yl Methyl Ketone* (**22**).—Methylmagnesium iodide in ether (0.7 cm^3, 0.36 mmol) [from methyl iodide (700 mg) and magnesium (110 mg) and standardised at 0.51 mmol MeMgI cm^{-3}] was added dropwise to a stirred solution of the bromo aldehyde (**19**) (73 mg, 0.28 mmol) in dry ether (1 cm^3) under argon at 20 °C. The mixture was stirred for 20 min, saturated aqueous ammonium chloride (4 cm^3) and ether (8 cm^3) were added, and the ether layer was washed with saturated brine (2 × 2 cm^3), dried ($MgSO_4$) and evaporated to give the alcohol (69 mg, 88%) (two diastereoisomers); $\nu_{max.}$ (neat film) 3 440br s cm^{-1}.

Chromium trioxide (270 mg, 2.70 mmol) was added to a stirred solution of pyridine (0.43 g, 5.4 mmol) in dry dichloromethane (10 cm^3) under argon at 20 °C. After this mixture had been stirred for 1 h, a solution of the foregoing alcohol (69 mg, 0.25 mmol) in dichloromethane (3 cm^3) was added (black tar immediately separated), and the mixture was stirred at 20 °C for 50 min. The product was added to ether (20 cm^3) and the solution was washed successively with dil. aqueous sodium carbonate (5 × 5 cm^3), dil. hydrochloric acid (4 × 5 cm^3), dil. aqueous sodium hydrogen carbonate (2 × 5 cm^3), and saturated brine (2 × 5 cm^3), and was then dried ($MgSO_4$). Evaporation of solvent gave a residue (66 mg) which was chromatographed on silica (50 g); elution with ether–light petroleum (3:17) gave the *ketone* (**22**) (57 mg, 82%) as an oil (Found: M^+, 276.0157 and 278.0135. $C_{14}H_{13}BrO$ requires M, 276.0150 [^{79}Br] and 278.0131 [^{81}Br]); $\nu_{max.}$ (neat film) 1 715s cm^{-1}; $\lambda_{max.}$ 202 and 279 nm (ε 21 500 and 8 700); δ_H 7.65—7.17 (5 H, m, 4 ArH and obscured 1 olefinic H), 6.26 (1 H, dd, J 10 and 1 Hz), 5.57 (1 H, d, J 10 Hz), 1.87 (3 H, s), and 1.76 (3 H, s); m/z 278 (M^+), 276 (M^+), 235, 233, and 153 (0.9, 0.9, 100, 100, and 60%).

2-[(E)-8-*Bromo-5-methyl-*5H-*benzocyclohepten-5-yl*]*vinyl Phenyl Ketone* (**20**).—To a stirred mixture of sodium hydride (55% dispersion in oil; 53 mg, 1.21 mmol) in dry DME (0.5 cm^3) under argon at 0 °C was added a solution of diethyl(2-oxo-2-phenylethyl)phosphonate (329 mg, 1.28 mmol) in DME (1 cm^3). After being stirred at 20 °C for 1 h, the mixture was treated with a solution of the bromoaldehyde (**19**) (50 mg, 0.19 mmol) in DME (1.5 cm^3), and was stirred at 20 °C for a further 2 h. After addition of ether (12 cm^3) the product was washed with water (5 × 2 cm^3), dried ($MgSO_4$), and evaporated. Chromatography of the crude residue (190 mg) on silica (50 g) in benzene–light petroleum (7:3) as eluant gave ketone (**20**) (43 mg total) contaminated with acetophenone. The product was added to water (10 cm^3) and steam-distilled to give *ca.* 50 cm^3 of distillate (*ca.* 20 min). The aqueous residue (*ca.* 35 cm^3) was extraced into dichloromethane (2 × 25 cm^3) and the combined extract was dried ($MgSO_4$) and evaporated. Chromatography of the crude product on silica (55 g) in dichloromethane–light petroleum (3:2) as eluant gave the pure *title compound* (**20**) (22 mg, 32%) as an oil (Found: M^+, 364.0464 and 366.0444. $C_{21}H_{17}BrO$ requires M, 364.0463 [^{79}Br] and 366.0444 [^{81}Br]); $\nu_{max.}$ (neat film) 1 667s, 1 648s, and 1 612s cm^{-1}; $\lambda_{max.}$ 203 and 259 nm (ε 26 800 and 16 000); δ_H 7.95—7.20 (10 H, m, 9 ArH and 1 obscured olefinic H), 6.59 (1 H, d, J 16 Hz, C=CHCOPh), 6.34 (1 H, dd, J 11 and 1.0 Hz), 6.29 (1 H, d, J 16 Hz, CH=CCOPh), 5.58 (1 H, d, J 11 Hz), and 1.77 (3 H, s); m/z 366 (M^+), 364 (M^+), 285, 180, 165, and 105 (3, 3, 13, 15, 19, and 100%).

5-*Methyl-*5H-*benzocyclohepten-5-yl Phenyl Ketone* (**35**).—Phenylmagnesium bromide in ether (6.0 cm^3, 1.8 mmol) [from bromobenzene (1.88 g) and magnesium (0.3 g) and standardised at 0.3 mmol PhMgBr cm^{-3}] was added to a stirred solution of the aldehyde (**29**) (0.3 g, 1.63 mmol) in dry ether (4 cm^3) under argon at 20 °C. The mixture was stirred for 20 min, saturated aqueous ammonium chloride (4 cm^3) and ether (8 cm^3) were added, and the ether layer was washed successively with saturated aqueous ammonium chloride (3 cm^3) and saturated brine (2 × 3 cm^3), and then dried ($MgSO_4$). Evaporation of solvent gave the alcohol (410 mg, 96%) (two diastereoisomers); $\nu_{max.}$ (neat film) 3 578br s and 3 460br s cm^{-1}.

A solution of dimethyl sulphoxide (306 mg, 3.92 mmol) in dichloromethane (4 cm^3) was added to a stirred solution of oxalyl chloride (248 mg, 1.95 mmol) in dry dichloromethane (3 cm^3) under argon at −55 °C. After the mixture had been stirred for 3 min, a solution of the foregoing alcohol (410 mg, 1.56 mmol) in dichloromethane (3 cm^3) was added. The mixture was stirred at −55 °C for 20 min, triethylamine (0.87 g, 8.6 mmol) was added, and the mixture was stirred at −55 °C for 5 min and then allowed to attain room temperature. Water (8 cm^3) was added and the product was extracted into ether (15 cm^3). The extract was washed successively with dil. hydrochloric acid (3 cm^3), dil. aqueous sodium hydrogen carbonate (3 cm^3), and saturated brine (2 × 3 cm^3). Drying ($MgSO_4$), and evaporation of solvent, gave a residue (430 mg) which was chromatographed on silica (75 g); elution with benzene gave the *title compound* (**35**) (366 mg, 90%) as a pale yellow oil (Found: M^+, 260.1201. $C_{19}H_{16}O$ requires M, 260.1201); $\nu_{max.}$ 1 680s cm^{-1}; $\lambda_{max.}$ 217, 240sh, and 270sh nm (ε 12 300, 10 000, and 6 700); δ_H 7.95—7.00 (9 H, m, ArH), 6.87 (1 H, d, [wffs], J 11 Hz), 6.40—6.00 (2 H, two overlapping m), 5.84 (1 H, d, J 9 Hz), and 2.03 (3 H, s); m/z 260 and 155 (4 and 100%).

5-*Methyl-5-vinyl-*5H-*benzocycloheptene* (**32**).—To a stirred slurry of methyltriphenylphosphonium bromide (325 mg, 0.91 mmol) in dry ether (35 cm^3) under argon at 0 °C was added n-butyl-lithium in hexane (1.3M; 0.7 cm^3, 0.91 mmol). The mixture was stirred for 2 h, a solution of the aldehyde (**29**) (120 mg, 0.65 mmol) in ether (2 cm^3) was added, and, after being stirred for 90 min, the mixture was stored at 0 °C (17 h). The reaction was quenched with water (20 cm^3) and the ether layer was washed with water (2 × 10 cm^3), and dried ($MgSO_4$). Evaporation of solvent gave the crude product (170 mg) which was chromatographed on silica (55 g); elution with light petroleum gave the *title compound* (**32**) (20 mg, 17%) as an oil (Found: M^+, 182.1093. $C_{14}H_{14}$ requires M, 182.1095); $\nu_{max.}$ (neat film) 3 025m, 1 632w, 1 484m, 1 457m, 1 368m, 911m, 799m, 778m, 753s, and 693s cm^{-1}; $\lambda_{max.}$(EtOH) 204 and 277 nm (ε 17 700 and 6 300); $\delta_H(CDCl_3)$ 7.70—7.10 (4 H, m, ArH), 7.02 (1 H, d [wffs], J 10.5 Hz), 6.35 (1 H, dd [wffs], J 10.5 and 6 Hz), 6.13 (1 H, dd [wffs], J 10 and 6 Hz), 5.66 (1 H, dd, J 17 and 10 Hz), 5.57 (1 H, d, [wffs], J 10 Hz), 4.83 (1 H, dd, J 10 and 1.5 Hz), 4.58 (1 H, dd, J 17 and 1.5 Hz), and 1.61 (3 H, s); m/z 182, 181, 167, 166, 165, 152, and 128 (47, 24, 100, 23, 41, 32, and 23%).

(*Z*)- *and* (E)-5-*Methyl-5-styryl-*5H-*benzocycloheptene* (**33**).—To a stirred slurry of benzyltriphenylphosphonium chloride (762 mg, 1.96 mmol) in dry ether (65 cm^3) under argon at 20 °C was added n-butyl-lithium in hexane (1.3M; 1.3 cm^3, 1.69 mmol). The mixture was stirred for 2 h, a solution of the aldehyde (**29**) (180 mg, 0.98 mmol) in ether (5 cm^3) was added, and the mixture was stirred at 20 °C for a further 70 h. Water (15 cm^3) was added and the organic layer was washed with water (2 × 15 cm^3), dried ($MgSO_4$), and evaporated. Chromatography of the crude

product (0.7 g) on silica (135 g) in benzene–light petroleum (2:98) as eluant gave the (Z)-*title compound* (110 mg, 43%) as white plates (from ethanol), m.p. 50—51 °C (Found: C, 93.1; H, 7.0%; M^+, 258.1412. $C_{20}H_{18}$ requires C, 93.0; H, 7.0%; *M*, 258.1408); $\nu_{max.}$(CCl_4) 3 027m, 1 493w, 1 482w, 1 367w, 1 043w, 1 031w, and 700s cm^{-1}; $\lambda_{max.}$ 206 and 278sh nm (ε 27 200 and 6 100); δ_H 7.65—6.70 (10 H, m, 9 ArH and 1 obscured olefinic H), 6.35 (1 H, dd, *J* 11 and 6 Hz), 6.28 (1 H, d, *J* 12 Hz), 5.91 (1 H, dd, *J* 10 and 6 Hz), 5.57 (1 H, d, *J* 10 Hz), 5.43 (1 H, d, *J* 12 Hz), and 1.66 (3 H, s); *m/z* 258, 243, 167, 165, 128, and 115 (100, 85, 93, 84, 63, and 89%).

Continued elution with benzene–light petroleum (2:98) gave the (E)-*title compound* (**33**) (67 mg, 26%) as an oil (Found: M^+, 258.1409); $\nu_{max.}$ (neat film) 3 020s, 1 600w, 1 496m, 1 482m, 1 449m, 1 044m, 964m, 800m, 778m, 750s, and 695s cm^{-1}; $\lambda_{max.}$ 204 and 252 nm (ε 27 300 and 15 300); δ_H 7.85—7.00 (9 H, m, ArH), 7.02 (1 H, d, *J* 11 Hz), 6.35 (1 H, dd, *J* 11 and 5.5 Hz), 6.16 (1 H, dd, *J* 11 and 5.5 Hz), 6.06 (1 H, d, *J* 17 Hz), 5.85 (1 H, d, *J* 17 Hz), 5.67 (1 H, d, *J* 11 Hz), and 1.71 (3 H, s); *m/z* 258, 243, 167, 165, 152, and 128 (100, 72, 59, 84, 23, and 51%).

Thermolysis of the Bromo Aldehyde (**19**).—The product of thermolysis of compound (**19**) was isolated from the solutions used for kinetic measurements. Thus four tubes each containing aldehyde (**19**) (14 mg, 0.053 mmol) in C_6D_6 (0.1 cm^3) [total 0.21 mmol of (**19**)] were heated for a period of six half-lives. Evaporation of solvent gave the crude product (55 mg) which was chromatographed on silica (20 g); elution with ether–light petroleum (1:9) gave *compound* (**38**; X = CHO, Y = Br) as an oil (26 mg, 46%) (Found: M^+, 261.9990 and 263.9975. $C_{13}H_{11}BrO$ requires *M*, 261.9994 [^{79}Br] and 263.9974 [^{81}Br]); $\nu_{max.}$ (neat film) 1 734s cm^{-1}; $\lambda_{max.}$ 224 and 281 nm (ε 10 700 and 5 200); δ_H 9.38 (1 H, s), 7.70—7.05 (4 H, m, ArH), 6.57 (1 H, d, [wffs], *J* 6 Hz), 6.05 (1 H, d [wffs], *J* 6 Hz) 4.31 (1 H, d, *J* 1 Hz), and 2.23 (3 H, d, *J* 0.7 Hz); *m/z* 264 (M^+), 262 (M^+), 235, 233, 183, and 153 (9, 9, 99, 100, 19, and 69%).

Thermolysis of the Bromo Nitrile (**21**).—A solution of the title compound (**21**) (32 mg, 0.12 mmol) in C_6D_6 (0.15 cm^3) was heated at 163 °C for 290 min. Evaporation of solvent gave the crude product (31 mg) which was chromatographed on silica (20 g); elution with ether–light petroleum (4:96) gave *compound* (**39**; X = CN, Y = Br) (16 mg, 50%) as pale yellow prisms (from ether–light petroleum), m.p. 109—111 °C (Found: C, 59.75; H, 4.0; N, 5.35%; M^+, 258.9995 and 260.9977. $C_{13}H_{10}BrN$ requires C, 60.0; H, 3.9; N, 5.4%; *M*, 258.9997 [^{79}Br] and 260.9977 [^{81}Br]); $\nu_{max.}$(CCl_4) 2 220m cm^{-1}; $\lambda_{max.}$ 206, 238, and 294 nm (ε 19 500, 10 700, and 7 800); δ_H($CDCl_3$) 7.90—7.15 (4 H, m, ArH), 6.24 (1 H, dd, *J* 11 and 1.0 Hz), 5.76 (1 H, dd, *J* 11 and 7 Hz), 2.90 (1 H, quintet [wffs], *J* 7 Hz), and 1.57 (3 H, d, *J* 7 Hz); *m/z* 261 (M^+), 259 (M^+), 246, 244, 180, 165, 153, and 152 (15, 18, 28, 30, 100, 23, 28, and 26%).

Continued elution with ether–light petroleum (4:96) gave *compound* (**38**; X = CN, Y = Br) (7 mg, 22%) as white crystals (from light petroleum), m.p. 120—121 °C (Found: M^+, 258.9992 and 260.9971. $C_{13}H_{10}BrN$ requires *M*, 258.9997 [^{79}Br] and 260.9977 [^{81}Br]); $\nu_{max.}$(CCl_4) 2 252vw cm^{-1}; $\lambda_{max.}$ 203, 219sh, and 278 nm (ε 8 050, 6 300, and 2 950); δ_H (400 MHz) 7.80—7.35 (4 H, m, ArH), 6.44 (1 H, br s, olefinic), 6.37 (1 H, d, *J* 6 Hz, olefinic), 4.90—4.10 (1 H, v br, HCCN), and 2.42 (3 H, s). The 400 MHz spectrum (and *cf.* the 90 MHz spectrum) show characteristics of slow 'ring-flip'; *m/z* 261 (M^+), 259 (M^+), 180, 153, and 152 (2, 2, 100, 18, and 18%).

Thermolysis of the Aldehyde (**29**).—A solution of the title compound (**29**) (40 mg, 0.22 mmol) in C_6D_6 (0.2 cm^3) was heated at 138 °C for 200 min. Evaporation of solvent gave the crude product (40 mg) which was chromatographed on silica (20 g); elution with benzene–light petroleum (7:3) gave an oil (34 mg) which, by n.m.r. spectroscopy, was shown to contain compound (**39**; X = CHO, Y = H) as the major product together with small amounts of starting material (**29**), the rearrangement product (**38**; X = CHO, Y = H), and a third (unidentified) aldehyde. The major product (**39**; X = CHO, Y = H) had $\nu_{max.}$ (neat film) 1 690s cm^{-1}; δ_H 9.80 (1 H, s), 7.90—7.10 (4 H, m, ArH), 7.27 (1 H, d, *J* 5 Hz), 6.27 (1 H, dd [wffs], *J* 10 and 5 Hz), 5.91 (1 H, dd, *J* 10 and 6 Hz), 2.71 (1 H, m), and 1.56 (3 H, d, *J* 7 Hz). A portion (24 mg) of the above product was dissolved in chloroform (0.3 cm^3) and was added to a stirred solution of hydroxylamine hydrochloride (50 mg, 0.72 mmol) in ethanol (1 cm^3) containing water (0.2 cm^3). Pyridine (57 mg, 0.72 mmol) was added and, after being stirred at 20 °C for 75 min, the solution was added to ether (5 cm^3) and the mixture was washed successively with dil. hydrochloric acid (3 × 1 cm^3), dil. aqueous sodium hydrogen carbonate (2 × 1 cm^3), and water (2 cm^3). Drying ($MgSO_4$), and evaporation of solvent, gave a residue (24 mg) which was chromatographed on silica (20 g); elution with ether–benzene (1:19) gave the pure *oxime* of aldehyde (**39**; X = CHO, Y = H) (17 mg, 65%) as white prisms (from dichloromethane–light petroleum), m.p. 118—119 °C (Found: C, 78.2; H, 6.65; N, 7.15%; M^+, 199.0997. $C_{13}H_{13}NO$ requires C, 78.4; H, 6.6; N, 7.0%; *M*, 199.0997); $\nu_{max.}$(CCl_4) 3 600sh s and 3 315br m cm^{-1}; $\lambda_{max.}$ 204, 240, and 287 nm (ε 14 100, 9 700, and 8 500); δ_H 8.12 (1 H, d, *J* 0.7 Hz, CH=N), 7.71 (1 H, m, ArH), 7.55—7.10 (3 H, m, ArH), 7.35 (1 H, s, OH), 6.77 (1 H, d, [wffs], *J* 5 Hz), 6.08 (1 H, ddd, *J* 10, 5, and 1.5 Hz), 5.70 (1 H, dd, *J* 10 and 5.5 Hz), 2.77 (1 H, m), and 1.57 (3 H, d, *J* 7 Hz); *m/z* 199, 181, 167, and 166 (12, 45, 36, and 100%).

Thermolysis of the Nitrile (**34**).—A solution of the title compound (**34**) (24 mg, 0.13 mmol) in C_6D_6 (0.15 cm^3) was heated at 138 °C for 22.3 h. Evaporation of solvent gave the crude product (24 mg) which was chromatographed on silica (40 g); elution with benzene–light petroleum (4:6) gave a mixture (20 mg, 83%) of products (**39**; X = CN, Y = H) (major) and (**38**; X = CN, Y = H) (minor) (7:1 from n.m.r. integrals) (Found: M^+, 181.0892. Calc. for $C_{13}H_{11}N$: *M*, 181.0891). Crystallisation (from light petroleum) gave white needles which were shown by n.m.r. spectroscopy to contain both products. Crystallisation from methanol also failed to separate the two isomers.

The major product (**39**; X = CN, Y = H) had $\nu_{max.}$(CCl_4) 2 217m cm^{-1}; δ_H(C_6D_6) 7.84 (1 H, m, ArH), 7.35—6.75 (3 H, m, ArH), 6.65 (1 H, d, *J* 5 Hz), 5.45 (1 H, dd [wffs], *J* 10 and 5 Hz), 5.24 (1 H, dd, [wffs], *J* 10 and 5.5 Hz), 2.22 (1 H, m), and 1.06 (3 H, d, *J* 7 Hz). The minor product (**38**; X = CN, Y = H) had δ_H(C_6D_6) (*inter alia*) 3.30 (1 H, d, *J* 5 Hz) and 1.98 (3 H, br s, Me); *m/z* (of the mixture of isomers) 181, 166, 153, and 140 (46, 100, 11, and 16%).

Thermolysis of the Benzoylacetylene (**31**).—(*a*) A solution of the title compound (**31**) (14 mg, 0.05 mmol) in C_6D_6 (0.1 cm^3) was heated at 100 °C for 45 min. Evaporation of solvent gave a residue (14 mg) which was chromatographed on silica (20 g); elution with ether–light petroleum (1:19) gave *compound* (**38**; X = C≡CCOPh, Y = H) (11 mg, 79%) as an oil (Found: M^+, 284.1201. $C_{21}H_{16}O$ requires *M*, 284.1201); $\nu_{max.}$ (neat film) 2 208s and 1 644s cm^{-1}; $\lambda_{max.}$ 203 and 261 nm (ε 26 300 and 16 600); δ_H 8.19 (2 H, m, ArH), 7.90—7.20 (7 H, m, ArH), 6.49 (1 H, d [wffs], *J* 5 Hz), 6.06 (1 H, dd [wffs], *J* 10 and 5 Hz), 5.78 (1 H, dd, *J* 10 and 6 Hz), 3.92 (1 H, d [wffs], *J* 6 Hz), and 2.42 (3 H, s); *m/z* 284, 269, 252, 241, 239, and 179 (100, 12, 10, 31, 25, and 37%).

(*b*) A solution of the title compound (33 mg, 0.12 mmol) in C_6D_6 (0.1 cm^3) was heated at 139 °C for 35 min. Evaporation of solvent gave a residue (32 mg) which was chromatographed on

silica (20 g); elution with benzene–light petroleum (3:2) gave a mixture of compounds (**38**; X = C≡CCOPh, Y = H) and (**39**; X = C≡CCOPh, Y = H) (6 mg, 18%), followed by pure *isomer* (**39**; X = C≡CCOPh, Y = H) (19 mg, 58%) as a pale yellow oil (Found: M^+, 284.1197. $C_{21}H_{16}O$ requires M, 284.1201); $\nu_{max.}$ (neat film) 2 185s and 1 637s cm^{-1}; $\lambda_{max.}$ 202, 266, and 334 nm (ε 23 020, 12 800, and 9 200); δ_H 8.19 (2 H, m, ArH), 7.94 (1 H, m, ArH), 7.80—7.15 (7 H, m, 6 ArH and 1 obscured olefinic H), 6.13 (1 H, dd [wffs], J 10 and 5.5 Hz), 5.80 (1 H, dd, J 11 and 5.5 Hz), 2.84 (1 H, m), and 1.57 (3 H, d, J 7 Hz); m/z 284, 269, 241, and 207 (100, 32, 44, and 37%).

Thermolysis of the Acetylene (**23**).—A solution of the title compound (**23**) (15 mg, 0.08 mmol) in C_6D_6 (0.1 cm^3) was heated at 145 °C for 210 min. Evaporation of solvent gave a residue (15 mg) which was chromatographed on silica (40 g); elution with benzene–light petroleum (1:19) gave a mixture (4 mg, 27%) of compounds (**39**; X = C≡CH, Y = H) (major) and (**24**) (minor) (ratio 12:1 from n.m.r. signals) (Found: M^+, 180.0938. Calc. for $C_{14}H_{12}$: M, 180.0939). The major product (**39**; X = C≡CH, Y = H) had $\nu_{max.}$ (neat film) 3 287s cm^{-1}; δ_H 7.94 (1 H, m, ArH), 7.58—7.15 (3 H, m, ArH), 7.05 (1 H, d, J 5.5 Hz), 6.03 (1 H, ddd, J 10, 5.5, and 1.5 Hz), 5.68 (1 H, dd, J 10 and 5.7 Hz), 3.24 (1 H, s, C≡CH), 2.76 (1 H, m), and 1.55 (3 H, d, J 7 Hz).

The mixture of products (an oil) could not be separated by crystallisation; m/z (of the mixture) 180, 165, 152, and 139 (37, 100, 10, and 11%).

Thermolysis of the Acetylene (**24**).—A solution of the title compound (**24**) (9 mg, 0.05 mmol) in C_6D_6 (0.1 cm^3) was heated at 130 °C for 170 min. Evaporation of solvent gave a residue (8 mg) which was chromatographed on silica (40 g); elution with dichloromethane–light petroleum (1:19) gave a mixture (4 mg, 44%) of compound (**39**; X = C≡CH, Y = H) (major) and starting material (**24**) (*ca.* 10:1 from n.m.r. integrals). The mixture was identical (n.m.r., i.r., t.l.c.) with that described above from the thermolysis of compound (**23**).

Thermolysis of the Ester (**17**).—A solution of the title compound (33 mg, 0.11 mmol) in C_6D_6 (0.1 cm^3) was heated at 205 °C for 2 h. Evaporation of solvent gave a residue (29 mg) which was chromatographed on silica (55 g); elution with benzene–light petroleum (9:1) gave methyl 2-bromo-1a,7b-dihydro-1-methyl-1*H*-cyclopropa[*a*]naphthalene-1-carboxylate (**44**) (14 mg, 42%), contaminated with a small amount of an unknown naphthalene. Crystallisation from light petroleum gave a pure sample of ester (**44**) as fine white needles, m.p. 74—77 °C (Found: M^+, 292.0099 and 294.0076. $C_{14}H_{13}BrO_2$ requires M, 292.0099 [^{79}Br] and 294.0079 [^{81}Br]); $\nu_{max.}$(CCl_4) 1 723 cm^{-1}; δ_H 7.38—6.95 (4 H, m, ArH), 6.90 (1 H, br s, olefinic), 3.79 (3 H, s, CO_2Me), 3.20 (1 H, d, J 9 Hz), 3.00 (1 H, dd, J 9 and 0.7 Hz), and 0.84 (3 H, s, Me); m/z 294 (M^+), 292 (M^+), 262, 260, 235, 233, 213, 185, and 153 (8, 8, 9, 9, 13, 15, 69, 19, and 100%).

Thermolysis of the 5-Benzoylbenzocycloheptene (**35**).—A solution of the title compound (37 mg, 0.14 mmol) in C_6D_6 (0.1 cm^3) was heated at 160 °C for 335 min. Evaporation of solvent gave a residue (34 mg) which was chromatographed on silica (22 g); elution with benzene–light petroleum (7:3) gave α-(1-*naphthyl*)*propiophenone* (**45**) (23 mg, 62%) as white needles (from light petroleum–dichloromethane), m.p. 132—134 °C (Found: C, 87.55; H, 6.15%; M^+, 260.1207. $C_{19}H_{16}O$ requires C, 87.7; H, 6.2%; M, 260.1201); $\nu_{max.}$(CCl_4) 1 690s cm^{-1}; $\lambda_{max.}$(EtOH) 227, 239, 271sh, and 281 nm (ε 20 100, 11 900, 7 350, and 7 800); δ_H(400 MHz) 8.25 (1 H, br d, J 8.5 Hz, naphthalene), 7.89 (1 H, d [wffs], J 8 Hz, naphthalene), 7.86 (2 H, m, Ph), 7.72 (1 H, br d, J 8.6 Hz, naphthalene), 7.63 (1 H, ddd, J 8.5, 7, and 1.5 Hz, naphthalene), 7.54 (1 H, ddd, J 8, 7, and 1.1 Hz, naphthalene), 7.41 (1 H, m, Ph), 7.33 (1 H, dd, J 8.6 and 7.5 Hz, naphthalene), 7.27 (2 H, m, Ph), 7.20 (1 H, dd, J 7.5 and 1.2 Hz, naphthalene), 5.39 (1 H, q, J 7 Hz, C*H*COPh), and 1.64 (3 H, d, J 7 Hz, Me); m/z 260, 155, 128, and 105 (16, 48, 6, and 100%).

Thermolysis of the (E)-*Benzoylvinyl Compound* (**20**).—A solution of the title compound (17 mg, 0.05 mmol) in C_6D_6 (0.1 cm^3) was heated at 100 °C for 45 min. Evaporation of solvent gave a residue (14 mg) which was chromatographed on silica (20 g); elution with benzene–light petroleum (7:3) gave *compound* (**40**) (7 mg, 41%) as a pale yellow oil (Found: M^+, 364.0466 and 366.0446. $C_{21}H_{17}BrO$ requires M, 364.0463 [^{79}Br] and 366.0444 [^{81}Br]); $\nu_{max.}$ (neat film) 1 683s cm^{-1}; $\lambda_{max.}$ 202 and 239 nm (ε 28 700 and 10 700); δ_H(C_6D_6) 7.90—7.60 (2 H, m, ArH), 7.45—6.80 (7 H, m, ArH), 5.76 (1 H, dd, J 7 and 1.6 Hz, olefinic), 3.85 (1 H, quad, J *ca.* 2 Hz), 3.09 (1 H, t, J *ca.* 2 Hz), 1.91 (1 H, dt, J 7 and *ca.* 2 Hz), 1.62 (1 H, t, J 7 Hz), and 1.29 (3 H, s, Me); irradiation of the signal at δ_H 3.85 causes (i) the signal at δ_H 5.76 to collapse to a doublet (J 7 Hz); (ii) the signal at δ_H 3.09 to collapse to a doublet J *ca.* 2 Hz; (iii) the removal of one 2-Hz coupling from the signal at δ_H 1.91; and (iv) no change to the signal at δ_H 1.62; m/z 366 (M^+), 364 (M^+), 285, 180, 165, and 105 (2, 2, 3, 9, 11, and 100%).

Thermolysis of the 5-Vinyl-5H-benzocycloheptene (**32**).—A solution of the title compound (**32**) (16 mg, 0.09 mmol) in C_6D_6 (0.1 cm^3) was heated at 100 °C for 7 h. Evaporation of solvent gave a residue (14 mg) which was chromatographed on silica (40 g); elution with light petroleum gave *compound* (**41**) (12 mg, 75%) as white needles (from methanol–dichloromethane), m.p. 50—52 °C (Found: M^+, 182.1097. $C_{14}H_{14}$ requires M, 182.1095); $\nu_{max.}$(CCl_4) 2 930s, 1 490m, 1 099m, 1 012m, 979m, and 708m cm^{-1}; δ_H (400 MHz), 7.41 (1 H, dm, J 7 Hz, ArH), 7.26—7.07 (3 H, m, ArH), 5.85 (1 H, ddt, J 9, 7.5, and 1.5 Hz), 5.67 (1 H, dd, J 9 and 6.5 Hz), 3.26 (1 H, dq, J 7.5 and 3 Hz), 1.95 (1 H, dq, J 8 and 3 Hz), 1.88 (1 H, ddt, J 8, 6.5, and 1.5 Hz), 1.64 (3 H, s, Me), 1.54 (1 H, ddt, J 11.5, 3, and 1.5 Hz), and 1.42 (1 H, dt, J 11.5 and 3 Hz); m/z 182, 167, 166, 165, and 152 (67, 100, 22, 39, and 27%).

Thermolysis of the (E)-*Styryl-5H-benzocycloheptene* (**33**).—A solution of the title compound (17 mg, 0.07 mmol) in C_6D_6 (0.1 cm^3) was heated at 90 °C for 4.5 h. Evaporation of solvent gave a residue (16 mg) which was chromatographed on silica (22 g); elution with dichloromethane–light petroleum (2:98) gave *compound* (**42**) (13 mg, 76%) as an oil (Found: M^+, 258.1414. $C_{20}H_{18}$ requires M, 258.1408); $\nu_{max.}$ (neat film) 2 935s, 1 600m, 1 490s, 1 451s, 1 349m, 1 079m, 1 032m, 808m, 756s, 727s, and 700s, cm^{-1}; δ_H (400 MHz), 7.46 (2 H, m, ArH), 7.36—7.05 (7 H, m, ArH), 5.79 (1 H, dd, J 10 and 8 Hz), 5.56 (1 H, dd, J 10 and 8 Hz), 3.36 (1 H, dt, J 8 and 3 Hz), 2.96 (1 H, br s), 2.18 (1 H, t, J 8 Hz), 2.12 (1 H, dt, J 8 and 3 Hz), and 1.75 (3 H, s, Me); m/z 258, 243, 228, 215, 167, and 165 (100, 62, 18, 12, 47, and 63%).

Thermolysis of the 5-Acetyl-5H-benzocycloheptene (**22**).—A solution of the title compound (28 mg, 0.1 mmol) in C_6D_6 (0.1 cm^3) was heated at 175 °C for 110 min. Evaporation of solvent gave a residue (27 mg) which was chromatographed on silica (20 g); elution with ether–light petroleum (3:17) gave a *naphthalene* [probably (**43**)] (6 mg, 21%) as an oil (Found: M^+, 276.0153 and 278.0138. $C_{14}H_{13}OBr$ requires M, 276.0150 [^{79}Br] and 278.0131 [^{81}Br]); $\nu_{max.}$ (neat film) 1 716s cm^{-1}; $\lambda_{max.}$ 228, 272sh and 281 nm (ε 47 700, 4 700, and 5 000; δ_H (400 MHz), 8.14 (1 H, br s, naphthalene), 7.75 (2 H, m, naphthalene), 7.60 (1 H, br s, naphthalene), 7.49 (2 H, m, naphthalene), 4.41 (1 H, q, J 7 Hz), 2.14 (3 H, s, COMe), and 1.48 (3 H, d, J 7 Hz, Me); m/z 278 (M^+),

276 (M^+), 235, 233, 197, and 154 (10, 10, 82, 82, 88, and 100%).

Continued elution with ether–light petroleum (3:17) gave a mixture (4 mg, 14%) of the rearrangement product (**38**; X = COMe), Y = Br) and a second naphthalene (Found: M^+, 276.0153 and 278.0137. Calc. for $C_{14}H_{13}BrO$: M, 276.0150 [^{79}Br] and 278.0131 [^{81}Br]). The compound (**38**; X = COMe, Y = Br) had δ_H (400 MHz) (*inter alia*) 6.44 (1 H, d quint, J 6 and 1.3 Hz) and 6.04 (1 H, d quart, J 6 and 1.5 Hz). The naphthalene had δ_H (400 MHz) (*inter alia*) 4.38 (1 H, q, J 7 Hz), and 1.55 (3 H, d, J 7 Hz. Me). The mixture had $\nu_{max.}$ (neat film) 1 715s cm^{-1}.

Cross-over Experiment.—A solution of a mixture of compounds (**21**) (6.4 mg, 0.025 mmol) and (**29**) (1.7 mg, 0.009 mmol) in C_6D_6 (0.04 cm^3) was heated at 137 °C for 12 h. The crude product (8 mg) was passed through a short column of silica (10 g) in ether–light petroleum (1:9). By t.l.c. and mass spectrometry, cross-over products were absent from the resulting product (7.5 mg).

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