The ^{13}C and ^{1}H N.M.R. Spectra of Homocubane, Norsnoutane and their 9-Keto- and 9,9-Ethylenedioxy-derivatives, and a Novel Route to Functionalised Brendanes [1]

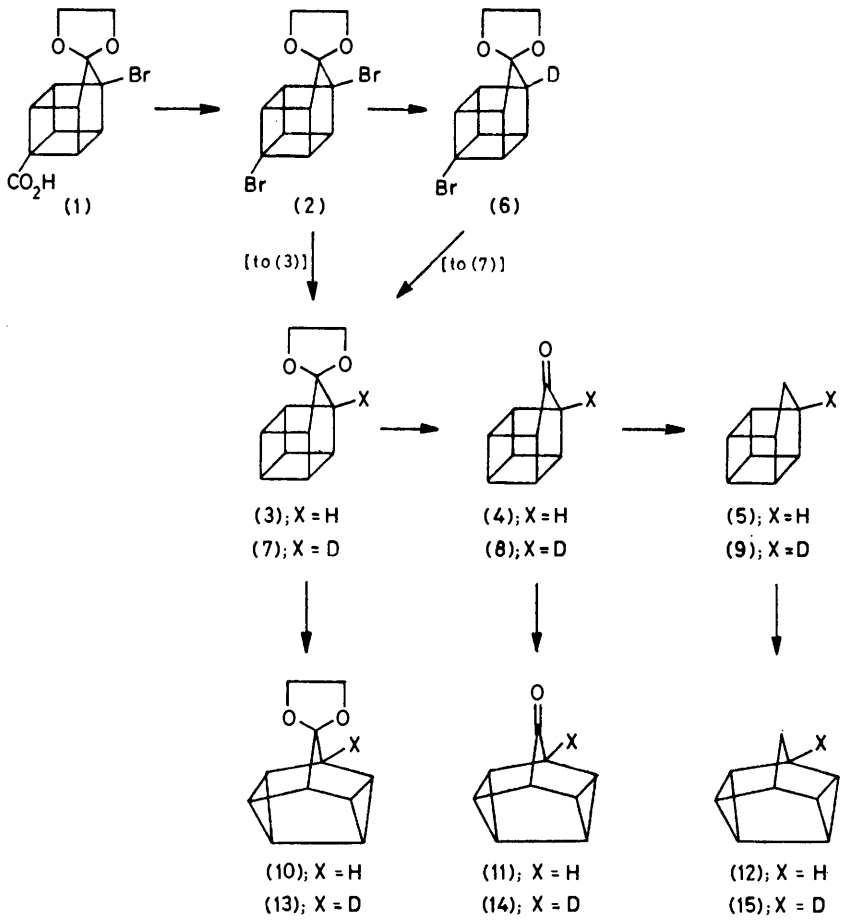
By John E. Hamlin and Kenneth J. Toyne,* Department of Chemistry, The University, Hull, HU6 7RX

The ^{13}C and ^{1}H n.m.r. spectra of homocubane (pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane) (5), norsnoutane (pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane) (12) and their 9-keto- and 9,9-ethylenedioxy-derivatives have been analysed using deuterium labelling. The protons α to the carbonyl or acetal group and the carbon atoms bearing these protons show unusual absorptions. The substituent effects in homocubanes and norbornanes are similar and no significant additional effect is apparent in the cage structure; the effect of the *endo*-annulated cyclopropane rings in the norsnoutanes is discussed. The hydrochloric acid-catalysed rearrangement of 9,9-ethylenedioxypentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (10) gives the brendane derivative, *exo*-2-chlorotricyclo[4.2.1.0^{3,7}]non-4-en-8-one (16).

SEVERAL years ago it was noted that the acetal and carbonyl derivatives of some polycyclic caged hydrocarbons exhibit a peculiar feature in their ^{1}H n.m.r. spectra.[2,3] In these derivatives the protons α to the acetal or the carbonyl group absorb at higher field than the corresponding protons in the parent hydrocarbon, whereas normally the presence of these functional groups causes a downfield shift for the α-protons. As yet, no satisfactory explanation for this peculiarity has been provided and in an attempt to define the generality of these effects we planned to study the n.m.r. spectra of a range of related caged systems. In this paper we start by reporting an analysis of the ^{13}C and ^{1}H n.m.r. spectra for the homocubane and norsnoutane systems, and we discuss an interesting rearrangement of the latter system to a brendane derivative.

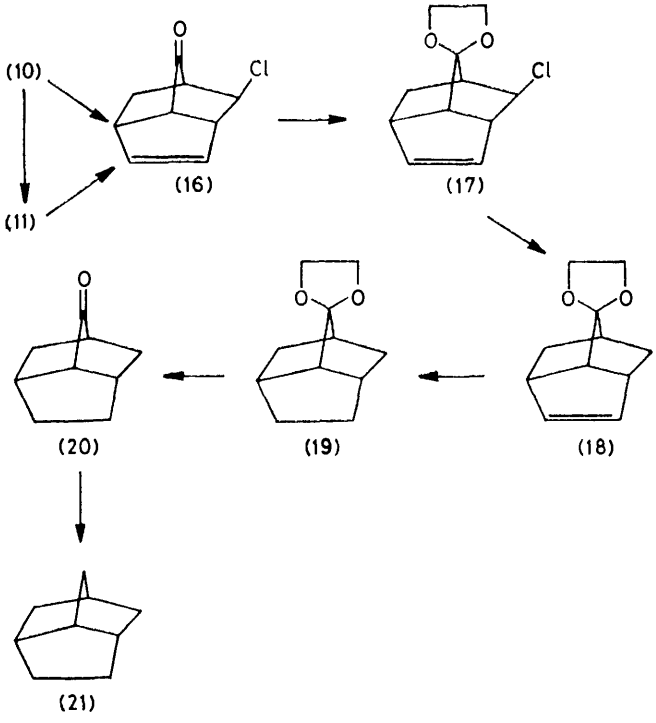
RESULTS AND DISCUSSION

The homocubane compounds [(3), (4), (5) and (7), (8), (9)] were prepared by the route shown in Scheme 1.

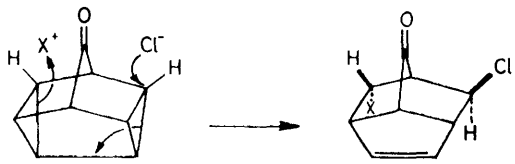


Treatment of compound (2) with butyl-lithium specifically removes the bromo-substituent adjacent to the acetal group and treatment of the anion with D_2O gives compound (6). Lithiation of (2) with 1 mol or with an excess of butyl-lithium occurs at C-1 rather than C-4, presumably because the anion at C-1 is more stabilised by the presence of the acetal group. The C-4 bromine (in the absence of the C-1 bromine) can, however, be exchanged by using t-butyl-lithium.[4] Both bromo-substituents in compound (2) and the bromo-substituent in compound (6) are efficiently removed by using Li–Bu^{t}OH–THF.

The norsnoutane (pentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]nonane) derivatives were prepared from the homocubanes by a silver(I)-catalysed rearrangement (Scheme 1). An attempt to prepare compound (11) from compound (10) by hydrolysis of the acetal group revealed an interesting and potentially useful rearrangement (Scheme 2). Compound (10) was hydrolysed to the ketone (11) by using a toluene-*p*-sulphonic acid catalyst, but with 6N-hydrochloric acid the product was *exo*-2-chlorotricyclo-[4.2.1.$0^{3,7}$]non-4-en-8-one (16). G.l.c. analysis of the



progress of the hydrochloric acid-catalysed reaction showed only three peaks, attributable to (10), (11), and (16), indicating that the rearrangement occurs after the initial hydrolysis of (10) to (11) or that the acetal of (16) is hydrolysed faster than it is formed from (10); (16) was also prepared directly from (11). The structure of (16) was confirmed by the sequence of reactions shown in Scheme 2 which finally yields brendane (tricyclo-[4.2.1.$0^{3,7}$]nonane). The rearrangement probably occurs as shown to give *endo*-X by edge protonation of a cyclopropane bond [5] followed by *exo*-attack of chloride ion. The stereochemistry of the product was confirmed by the use of a shift reagent and double-resonance techniques on the product from the hydrochloric acid reaction, and on that from a reaction using 6N-DCl–cyclohexane. The principal observations were that deuteriation causes the disappearance of the sharp doublet at δ 1.54 and the proton remaining on C-9 is more influenced by the shift reagent than the proton on C-2. The preparation of (16)



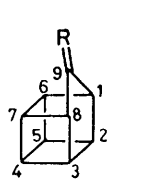
permits the synthesis of brendane derivatives with substituents at the 2-, 4-, 5-, and 8-positions, and is a useful alternative to other routes to brendanes.[6-8]

^{13}C *and* ^{1}H *N.M.R. Spectra* (*see Table* 1).—The chemical shift of C-9 in homocubane (5) is 7.2 p.p.m. downfield from the signal for C-7 in norbornane. Two significant differences between norbornane and (5) are the greater total strain energy of (5) (121.8 kcal mol^{-1} compared with 16.8 kcal mol^{-1} for norbornane [9]) and the presence in homocubane of the C-4 and C-5 atoms. However, the values of ^1J(CH) for C-1 and C-9 in homocubane indicate that these atoms experience similar strain to the C-1 and C-7 atoms, respectively, in norbornane (see Table 1). The substituent effect of a 2-*endo*-methyl group in norbornane is to shift the C-7, C-1, and C-4 resonances downfield by 2.0, 5.4, and 1.4 p.p.m., respectively [10] and so the simple view of homocubane as a norbornane structure with *endo*-substituents would indicate chemical shifts similar to those observed for the C-1 and C-9 atoms, and there seems to be no reason to invoke substantial effects peculiar to caged systems.

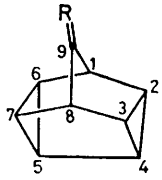
For norsnoutane (12), the values of ^1J(CH) at C-1 and C-9 (see Table 1) are very similar to those for the corresponding atoms in norbornane and homocubane, and on that basis one might expect the chemical shifts of C-1 and C-9 to be similar in (5) and (12). For C-1 this is true but the C-9 resonance in (12) is moved markedly downfield. A cyclopropane ring annulated in an *endo*-fashion to a norbornane system has a deshielding effect on the methano-bridge [11,12] which is thought to operate by charge transfer from the C–C σ-bonds of the methano-bridge to the antibonding Walsh orbital A^1_2 of the cyclopropane ring. The effect is not apparent for an ethano-bridge (see Figure) and it has been suggested that this is because of back-donation from the bonding Walsh orbital E' of the cyclopropane to the antibonding orbital of the ethano-bridge (CH_2–CH_2).[11] With two cyclopropane substituents, a shielding effect has been observed for the ethano-bridge (−5.8 p.p.m.) and the values we report for (12) now show the effect of two similarly placed cyclopropane substituents on a methano-bridge. [The deshielding in (24) is attributed to the effect of the C-4–

TABLE 1

N.m.r. data for homocubanes and norsnoutanes [a]



(5); R = H_2
(4); R = O
(3); R =



(12); R = H_2
(11); R = O
(10); R = 

	^{13}C Chemical shifts					^{1}H Chemical shifts				
	C-1, -8	C-2, -3, -6, -7	C-4, -5	C-9	Other	H-1, -8	H-2, -3, -6, -7	H-4, -5	H-9	Other
(5) [c]	44.5	44.1	41.8	45.5		3.22	3.25	3.14	1.67	
(4)	44.1	39.1	45.8	221.5		3.03	3.69	3.59		
	(−0.4)	(−5.0)	(+4.0)	(+176.0)		(−0.19)	(+0.44)	(+0.45)		
(3)	46.1	42.2	42.2	128.9	Acetal 65.0	2.99	3.56	3.30		Acetal 3.91
	(+1.6)	(−1.9)	(+0.4)	(+83.4)		(−0.23)	(+0.31)	(+0.16)		
(12) [d]	42.4	40.2	38.2	59.7		2.56	1.98	2.10	1.88	
(11)	41.5	29.3	33.2	204.6		2.48	1.98	2.40		
	(−0.9)	(−10.9)	(−5.0)	(+144.9)		(−0.08)	(0.00)	(+0.30)		
(10)	45.6	34.0	35.0	135.8	Acetal 64.9	2.32	1.95	2.11		Acetal 3.95
	(+3.2)	(−6.2)	(−3.2)	(+76.1)		(−0.24)	(−0.03)	(+0.01)		
		C-1, -4	C-2, -3, -5, -6	C-7						
Norbornane [b,e,f]		36.3	29.6	38.3						
Norbornan-7-one [f]		37.8	24.2	216.8						
		(+1.5)	(−5.4)	(+178.5)						

[a] Shifts in δ/p.p.m. from internal $SiMe_4$ in $CDCl_3$; substituent chemical shifts in parentheses. [b] Ref. 14 gives 36.6 (C-1), 30.0 (C-2), 38.6 (C-7) for norbornane. [c] ^1J(CH) for C-1, C-2, C-4, and C-9 are 146, 152, 157, and 129 Hz, respectively (this work). [d] ^1J(CH) for C-1, C-2, C-4, and C-9 are 144, 174, 171, and 132 Hz, respectively (this work). [e] ^1J(CH) for C-1, C-2, and C-7 are 141, 131, 132 Hz, respectively (H-J. Schneider, W. Gschwendtner, D. Heiske, V. Hoppen, and F. Thomas, *Tetrahedron*, 1977, **33**, 1769). [f] See J. B. Stothers, J. R. Swenson, and C. T. Tan, *Can. J. Chem.*, 1975, **53**, 581.

C-5 bond connecting the two cyclopropane rings.] The methano-bridge resonance in (12) is moved considerably downfield and its shift difference from that of the ethano-bridge resonance in (24) (*i.e.* 27.2 p.p.m.) is *ca.* twice the shift difference of 14.9 p.p.m. [see (22) and (23)]

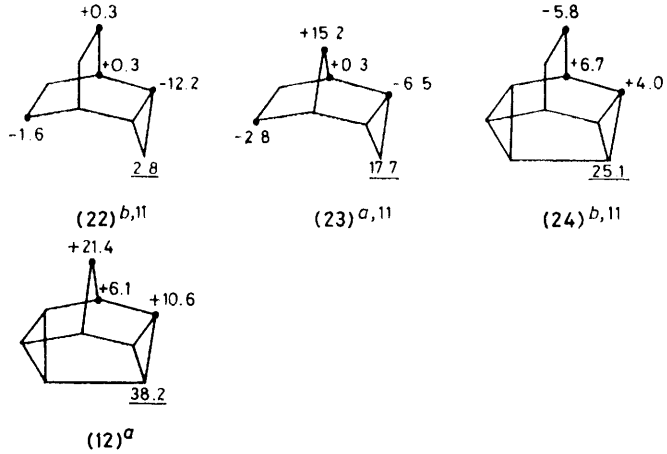


FIGURE Effect of cyclopropane annulation. Substituent-induced chemical shifts (Δδ/p.p.m.) relative to the parent system; *a*, norbornane; *b*, bicyclo[2.2.2]octane; underlined numbers are δ values.

for the presence of one cyclopropane ring. The resonance for the C-4(C-5) carbon in (12) is much further downfield (13.1 p.p.m.) than that for the corresponding atoms in (24) and this difference is similar to the difference (14.9 p.p.m.) for the *endo*-cyclopropyl methylenes in (22) and (23) and for other comparable pairs of compounds.[11]

Cyclobutane also has high-lying antibonding Walsh orbitals of the appropriate symmetry ($1A_{2g}$) [13] but it does not seem necessary to invoke their involvement to explain the downfield shift of C-9 in (5) relative to C-7 in norbornane (see above).

All the other carbon atoms in (12), being part of cyclopropane rings, resonate at higher field than the comparable carbons in (5) whose resonances have moved upfield (41.8 and 44.1 p.p.m.) from the value (δ 47.3) for cubane.[14] This upfield displacement may arise from a combination of changes in strain [see ^1J(CH) in Table 1; ^1J(CH) for cubane is 153.8 Hz [14]] and increased 1,5 and 4,8 interactions.

The most obvious result of the introduction of a carbonyl group into the homocubane or norsnoutane system is that the α-carbons (C-1 and C-8) in the ketone resonate at *higher* field than in the hydrocarbon, whereas normally a carbon atom α to a carbonyl group is shifted

strongly downfield.* This peculiar effect can be discussed by firstly assessing to what extent these systems differ from norbornane derivatives and then by attempting to understand the inherent peculiarity of the latter systems. In Table 2 we give the chemical-shift differences for the homocubane and norsnoutane derivatives relative to the norbornane derivatives

TABLE 2

^{13}C Chemical-shift differences (Δδ/p.p.m.) for homocubane and norsnoutane derivatives relative to norbornane derivatives

	Homocubane			Norsnoutane		
	C-1, -8	C-2, -3, -6, -7	C-9	C-1, -8	C-2, -3, -6, -7	C-9
Hydrocarbon	+8.2	+14.5	+7.2	+6.1	+10.6	+21.4
9-Ketone	+6.3	+14.9	+4.7	+3.7	+5.1	−12.2

Chemical shift for atoms in the caged system minus shift for corresponding atoms in norbornane or norbornan-7-one (see Table 1).

ences for the homocubane and norsnoutane derivatives relative to the norbornanes. The clear conclusion from this comparison is that the introduction of a carbonyl group into homocubane or norbornane has approximately the same effect, but for norsnoutane the change is significantly different at C-2, -3, -6, and -7, and vastly different at C-9. This effect can be explained on the basis of an interaction between the bonding Walsh orbitals on C-2,C-3 or C-6,C-7 with the π^*_{CO} orbital on C-9 in the ketone which will lead to an increased excitation energy for the C-2, -3, -6, -7, and -9 atoms [22] and so lead to increased paramagnetic shielding.[23] A further consequence of this cross-conjugation is that the carbonyl stretching frequency (in carbon tetrachloride) is greater in norsnoutanone (1 775 cm^{-1}) than in homocubanone (1 764 cm^{-1}).

The similar substituent effect of the carbonyl group in norbornan-7-one and homocubanone suggests that the peculiarities of the C-1,C-8 and H-1,H-8 resonances (see Table 2) may be a consequence not of caged systems but of the 1,4-methano-bridged boat-cyclohexane unit which is present in norbornane, homocubane, norsnoutane, and 1,4-bishomocubanes.[2] The explanation of the insensitivity of the C-1,C-8 or H-1,H-8 atoms to carbonyl substitution may involve many factors including geometry and hybridisation changes or unusual anisotropic effects,[2] rear-orbital overlap of the bridgehead-hydrogen bonds,[24,25] or the non-interaction of *p*-type orbitals on the bridging carbon atom.[26] We intend to analyse the ^{13}C and ^{1}H spectra for 1,3-bishomocubane and its carbonyl and ethylene acetal derivatives because these compounds do not have a plane of symmetry through the methylene bridge and the greater variety of absorbing nucleii may help to distinguish between the possible factors listed above.

* The substituent shift downfield lies within the range +11.0 to +23.6 p.p.m. for cyclobutanone,[15] cyclopentanone,[16] cyclohexanone,[16] bicyclo[3.2.1]octan-2-one, -3-one and -6-one,[16] bicyclo[3.3.1]nonan-9-one,[17] adamantanone,[18] bicyclo[2.2.2]-octan-2-one,[18] twistan-4-one,[19] bicyclo[3.2.2]nonan-6-one,[16] norbornan-2-one,[20] *exo*- and *endo*-tricyclo[3.2.1.0^{2,4}]octan-6-one;[21] the substituent shift for the carbonyl carbon atom is within the range δ +178.8 to +193.9 for these compounds.

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded at 100 MHz with a JEOL 4H-100 spectrometer and ^{13}C n.m.r. spectra were obtained with a Bruker HX-90 spectrometer operating at 22.63 MHz; in all cases tetramethylsilane was the internal standard and $CDCl_3$ was the solvent. The assignments for the ^{1}H and ^{13}C absorptions follow unambiguously from comparison of the spectra for protonated and deuteriated compounds, and by also employing the off-resonance mode for ^{13}C spectra. I.r. spectra were recorded by using a Perkin-Elmer 457 spectrophotometer. Mass spectra were recorded with an A.E.I. MS902 spectrometer. Combustion analyses of deuterium compounds were not obtained; all other compounds gave satisfactory analyses for carbon and hydrogen, and for bromine and chlorine when present.

Compound (2).—Bromine (19.2 g, 0.12 mol) in dry 1,2-dibromoethane (150 ml) was added with rapid stirring to compound (1) [3,27] (36.0 g, 0.12 mol) and mercury(II) oxide (26.1 g, 0.156 mol) in dry 1,2-dibromoethane (850 ml) and the mixture was refluxed for 6 h. The cooled solution was filtered and the filtrate was washed successively with water (2 × 500 ml), 10% sodium hydroxide (4 × 250 ml), and water (2 × 500 ml), and then dried ($MgSO_4$). Evaporation of the solvent and crystallisation (from ethanol) of the residue gave compound (2) (28.3 g, 54%), m.p. 137—140 °C (lit.,[28] 143—144 °C).

Compound (3).—This was prepared from compound (2) by using Bu^{t}OH–Li–THF as described previously for the preparation of pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane-6,10-dione bis(ethylene acetal).[3] Compound (3) (85%) had b.p. 75—77 °C/0.01 mmHg (lit.,[29] 85—87 °C/3.0 mmHg); δ_H ($CDCl_3$) 2.88—3.05 (m, 2 H), 3.16—3.36 (m, 2 H), 3.50—3.67 (m, 4 H), and 3.91 (s, 4 H); δ_C ($CDCl_3$) 128.94 (1 C), 64.99 (2 C), 46.14 (2 C), and 42.18 (6 C).

Compound (4).—This was prepared by hydrolysing compound (3) (10.0 g), by heating under reflux with 4N-hydrochloric acid (120 ml) and benzene (150 ml) for 24 h. The aqueous phase was replaced with fresh 4N-hydrochloric acid (120 ml) and the mixture was heated for a further 30 h. The organic layer was washed with water and dried ($MgSO_4$). Removal of the solvent and sublimation of the residue (60 °C/20 mmHg) gave compound (4) (78%), m.p. 73—74 °C (lit.,[30] 72—73 °C); δ_H ($CDCl_3$) 2.89—3.08 (m, 2 H), 3.45—3.62 (m, 2 H), and 3.62—3.81 (m, 4 H); δ_C ($CDCl_3$) 221.49 (1 C), 45.75 (2 C), 44.06 (2 C), and 39.12 (4 C).

Compound (5).—This was prepared by Wolff–Kishner reduction of compound (4). Sublimation (80 °C/atmospheric pressure) of the crude product and crystallisation (methanol) of the sublimate gave compound (5) (70%) as an extremely volatile, waxy solid; m.p. 107—108 °C (sealed tube) (lit.,[31] 107.5—108.5 °C); δ_H ($CDCl_3$) 1.67 (s, 2 H), 3.02—3.18 (m, 2 H), and 3.18—3.43 (m, 6 H); δ_C ($CDCl_3$) 45.49 (1 C), 44.52 (2 C), 44.13 (4 C), 41.79 (2 C).

Compound (6). Compound (2) (12.0 g, 0.036 mol) was dissolved in dry THF (200 ml) and cooled to −78 °C under dry nitrogen. Butyl-lithium (22.5 ml of a 2.4N solution in hexane, 0.0612 mol) was added dropwise, keeping the temperature below −40 °C. Deuterium oxide (5.0 g, 0.25 mol) was added dropwise and the reaction mixture was allowed to warm to room temperature. The mixture was diluted with water (150 ml) and washed with ether (3 × 200 ml). The ether washings were washed with water and dried ($MgSO_4$). Removal of the solvent gave a crude product which was distilled (103—105 °C [oil bath]/0.1 mmHg) to

give *compound* (6) (60%) as an oil which solidified on standing, m.p. 52—54 °C; δ_H ($CDCl_3$) 3.13 (t, 1 H), 3.50—3.88 (m, 5 H), and 3.85—3.99 (m, 4 H).

Compounds (7), (8), *and* (9).—These were prepared by using the procedures described above for the preparation of the protio-compounds (3), (4), and (5) respectively. *Compound* (7) (78%) had b.p. 73—76 °C (oil bath)/0.01 mmHg; δ_H ($CDCl_3$) 2.85—3.02 (m, 1 H), 3.15—3.32 (m, 2 H), 3.40—3.59 (m, 4 H), 3.91 (s, 4 H); δ_C ($CDCl_3$) 128.94 (1 C), 65.05 (2 C), 46.21 (1 C), 42.18 (6 C). *Compound* (8) (56%) had m.p. 73—74 °C; δ_H ($CDCl_3$) 2.95—3.01 (m, 1 H), 3.47—3.62 (m, 2 H), and 3.61—3.81 (m, 4 H); δ_C ($CDCl_3$) 221.62 (1 C), 45.75 (2 C), 44.06 (1 C), and 39.12 (4 C). *Compound* (9) (72%) had m.p. 107—108 °C (sealed tube); δ_H ($CDCl_3$) 1.67 (s, 2 H), 3.00—3.18 (m, 2 H), and 3.18—3.43 (m, 5 H); δ_C ($CDCl_3$) 45.36 (1 C), 44.45 (1 C), 44.06 (4 C), and 41.79 (2 C).

Compounds (10), (13), (11), (14), (12), and (15).—These were prepared by the $AgClO_4$–C_6H_6 (or C_6D_6)-catalysed rearrangement of the homocubanes (3), (7), (4), (8), (5), and (9), respectively.[4] *Compound* (10) (84%) had b.p. 86—89 °C (oil bath)/0.02 mmHg; δ_H ($CDCl_3$) 1.86—2.05 (m, 4 H), 2.05—2.26 (m, 2 H), 2.26—2.42 (m, 2 H), and 3.92 (s, 4 H); δ_C ($CDCl_3$) 135.76 (1 C), 64.93 (2 C), 45.62 (2 C), 35.03 (2 C), and 33.99 (4 C). *Compound* (13) (86%) had b.p. 80—85 °C (oil bath)/0.15 mmHg; δ_H ($CDCl_3$) 1.80—2.03 (m, 4 H), 2.03—2.18 (m, 2 H), 2.18—2.40 (m, 1 H), and 3.92 (s, 4 H); δ_C ($CDCl_3$) 135.54 (1 C), 64.81 (2 C), 45.53 (1 C), 34.98 (2 C), and 33.84 (4 C). *Compound* (11) (80%) had m.p. 87—88 °C; δ_H ($CDCl_3$) 1.89—2.10 (m, 4 H), 2.27—2.45 (m, 2 H), and 2.45—2.54 (m, 2 H); δ_C ($CDCl_3$) 204.59 (1 C), 41.46 (2 C), 33.21 (2 C), and 29.25 (4 C). *Compound* (14) (92%) had m.p. 90—92 °C; δ_H ($CDCl_3$) 1.92—2.06 (m, 4 H), 2.29—2.45 (m, 2 H), and 2.45—2.51 (m, 1 H); δ_C ($CDCl_3$) 204.53 (1 C), 41.39 (1 C), 33.19 (2 C), and 29.14 (4 C). Compound (12) (79%) had m.p. 87—88 °C (lit.,[4] 87—88 °C); δ_H ($CDCl_3$) 1.87 (t, 2 H), 1.91—2.03 (m, 4 H), 2.03—2.22 (m, 2 H), and 2.47—2.64 (m, 2 H); δ_C ($CDCl_3$) 59.73 (1 C), 42.44 (2 C), 40.16 (4 C), and 38.21 (2 C). *Compound* (15) (55%) had m.p. 81—83 °C; δ_H ($CDCl_3$) 1.87 (t, 2 H), 1.92—2.04 (m, 4 H), 2.04—2.22 (m, 2 H), and 2.48—2.64 (m, 1 H); δ_C ($CDCl_3$) 59.61 (1 C), 42.41 (1 C), 40.05 (4 C), and 38.15 (2 C).

exo-2-*Chlorotricyclo*[4.2.1.$0^{3,7}$]*non*-4-*en*-8-*one* (16).—Compound (10) (1.80 g, 0.010 mol), 6N-hydrochloric acid (50 ml), and benzene (50 ml) were stirred and refluxed for 6 h. The organic layer was washed with water and dried ($MgSO_4$). Removal of the solvent and distillation of the residue (b.p. 70—72 °C [oil bath]/0.07 mmHg) gave *compound* (16) (81%); *m/e* 168 (M^+), 105, 104, 103, 91, 78; $\nu_{max.}$ (film) 3 065, 2 965, 2 870, 1 798, 1 778, 1 607, 749, and 708 cm^{-1}; δ_H ($CDCl_3$) 1.54 (d, 1 H, *J* 13 Hz), 1.83—2.15 (m, 1 H), 2.41 (d, 1 H, *J* 5 Hz), 2.72—2.94 (m, 2 H), 3.04—3.18 (m, 1 H), 3.92 (s, 1 H), and 6.02—6.28 (m, 2 H); δ_C ($CDCl_3$) 212.97, 140.33, 133.67, 57.71, 53.41, 53.00, 52.03, 37.90, and 30.03.

Compound (17).—This was prepared from compound (16), ethylene glycol, and toluene-*p*-sulphonic acid catalyst in benzene by the usual procedure and had b.p. 90—93 °C [oil bath]/0.05 mmHg (82%); *m/e* 212 (M^+); δ_H ($CDCl_3$) 1.24 (d, 1 H, *J* 11 Hz), 1.97—2.22 (m, 1 H) 2.22—2.34 (m, 1 H), 2.58—2.78 (m, 2 H), 2.91—3.08 (m, 1 H), 3.77 (s, 1 H), 3.85—4.19 (m, 4 H), and 5.95—6.13 (m, 2 H).

Compound (18).—This was prepared from compound (17) by using the procedure described for the preparation of compound (3). Compound (18) (71%) had b.p. 50—55 °C [oil bath]/0.06 mmHg; *m/e* 178 (M^+); δ_H ($CDCl_3$) 1.21 (d, 2 H, *J* 11.3 Hz), 1.75—2.04 (m, 3 H), 2.47—2.74 (m, 3 H), 3.98 (s, 4 H), and 5.94 (s, 2 H); δ_C ($CDCl_3$) 137.93, 121.86, 64.73, 55.35, 44.27, 41.31, and 32.95.

Compound (19).—This was prepared by hydrogenation of compound (18) with 10% palladium-on-carbon in ethyl acetate. Compound (19) (83%) had b.p. 48—52 °C (oil bath)/0.06 mmHg; *m/e* 180; δ_H ($CDCl_3$) 0.79 (d, 2 H, *J* 9 Hz), 1.37—2.40 (m, 10 H), and 3.79 (s, 4 H); δ_C ($CDCl_3$) 122.80, 64.64, 50.32, 38.51, 37.90, 37.62, and 32.87.

Compound (20).—This was prepared from compound (19) by using a procedure similar to that described for the preparation of compound (4). Compound (20) (85%) was sublimed at 85—95 °C (oil bath)/12 mmHg, m.p. 99—101 °C; *m/e* 136; δ_H ($CDCl_3$) 1.05 (d, 2 H, *J* 11 Hz) and 1.52—2.73 (m, 10 H); δ_C ($CDCl_3$) 217.92, 48.94, 39.36, 36.12, and 34.41.

Tricyclo[4.2.1.$0^{3,7}$]*nonane* (*Brendane*) (21).—This was prepared from compound (20) by using the procedure described for the preparation of compound (5). Compound (21) was sublimed at 80—90 °C/atmospheric pressure (86%), m.p. 96—98 °C (sealed tube) (lit.,[6] 98—99 °C); δ_H ($CDCl_3$) 0.76 (d, 2 H, *J* 10.5 Hz), 1.41 (s, 2 H), and 1.49—2.33 (m, 10 H); δ_C ($CDCl_3$) 48.05, 40.91, 39.89, 39.00, 35.71, and 32.18.

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