Regioselective Transannular Cyclization of Deslongchamps's Diketone. New Entries to Polycyclic Cage Structures: Reductive Opening of a Cyclobutyl Ketone with Lithium in Liquid Ammonia and its Photochemical Rearrangement to a Bridged Cyclopentyl Ether

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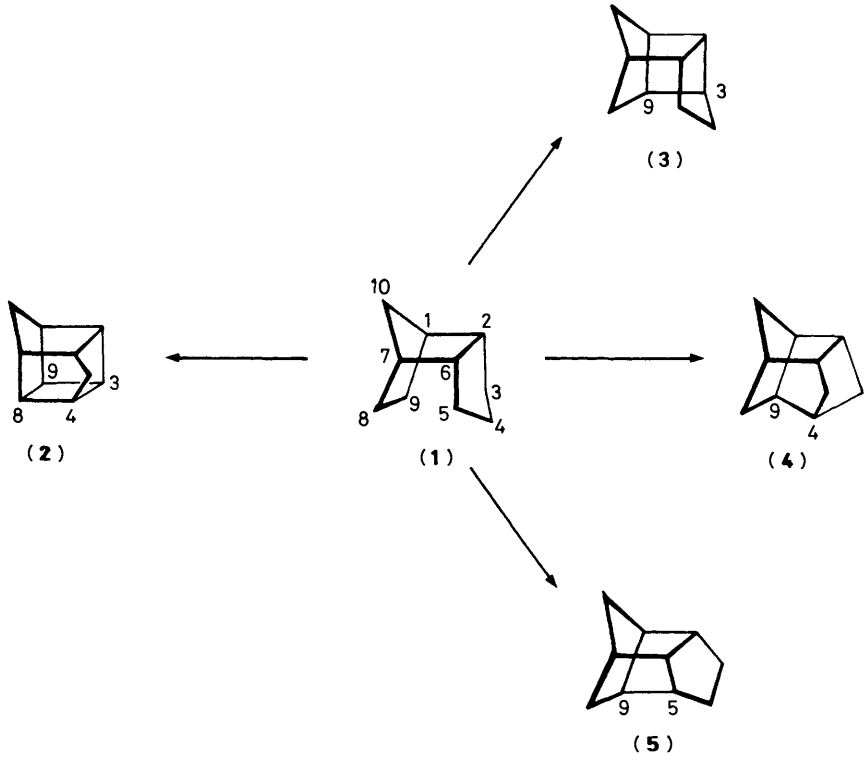
Regioselective bromination of Deslongchamps's diketone (**6**), followed by base-induced transannular cyclization, leads to tetracyclo[5.3.0.^{2,6}.0^{3,9}]decane-5,8-dione (**8**), together with minor amounts of the isomeric tetracyclo[5.2.1.0^{2,6}.0^{3,8}]decane-4,9-dione (**9**). The chemistry and photochemistry of the monoacetals of (**8**) have been studied, and structural assignments confirmed either by *X*-ray diffraction analysis or 2D n.m.r. spectroscopy.

Cage-structure compounds and their derivatives are of great interest in connection with a number of topics, such as the testing of the scope and limitations of synthetic methods, the determination of structure–reactivity relationships, and the theoretical and experimental estimation of strain energies.[1] More recently, the lipophilic character of spherical hydrocarbon molecules has led to additional interest in the pharmacological properties of these compounds.[2]

general strategy are found in the synthesis of bullvalene,[3] twistane,[4] cubane,[5] and dodecahedrane.[6]

In this context, properly functionalized derivatives having the skeleton of *endo*-tricyclo[5.2.1.0^{2,6}]decane (**1**) are of interest for the synthesis of tetra- and penta-cyclo C_{10} systems (Scheme 1).

Whereas photochemical intramolecular [2 + 2]cycloadditions of derivatives of compound (**1**) have been an important synthetic starting point for bis-homocubane (**2**) derivatives,[7]



Scheme 1.

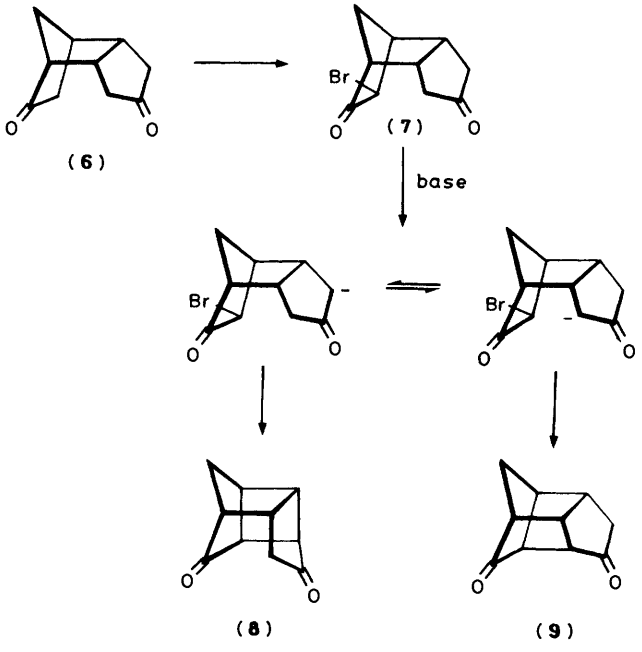
Since compounds with cage structures have usually a substantial amount of strain energy, a general strategy for the synthesis of these compounds relies on the preparation of key intermediates which have adequate geometry and functionalization in order to create, through some irreversible process, the bond(s) which mostly contribute to the total strain of the molecule by means of proximity effects. Examples of such a

nothing is known concerning the selective bond formation between C(3)–C(9), C(4)–C(9), and C(5)–C(9) which would lead to the tetracyclic skeletons (**3**), (**4**), and (**5**), respectively. In fact, derivatives of (**3**) and (**4**) have been obtained by selective reduction of one of the bonds of bishomocubane (**2**).[8] On the other hand, derivatives of (**5**), and even the hydrocarbon itself have been synthesized starting from an intermediate with the

exo-dicyclopentadiene skeleton.[1b] Hydrocarbon (**5**) has also been obtained by hydrogenation of one of the photoisomers of triquinacene.[9]

As a result of our studies on the regioselective functionalization of *endo*-dicyclopentadiene,[10] we have developed a highly efficient synthesis of Deslongchamps's diketone (**6**), a compound that meets the aforementioned requirements to become a key intermediate for the synthesis of compounds with skeletons (**3**), (**4**), and (**5**).

In particular, we thought that the irreversible formation of a bond between positions 3 and 9, and/or 5 and 9, could take place on an intermediate such as (**7**) by means of an intramolecular displacement of a good leaving group (a bromide, for instance) by an enolate anion generated either on position 3 or 5 (Scheme 2).



Scheme 2.

Although no regioselectivity of any kind should be expected in the enolate formation, there was the possibility that the cyclization of one of them would be more favoured and, accordingly, the regioselective formation of one of the two possible diketones (**8**) and (**9**) could be attained. We report here the results obtained on the base-induced cyclization of bromo diketone (**7**).

Results and Discussion

The bromo diketone (**7**) was easily prepared from the diketone (**6**) *via* the following sequence of reactions (see Scheme 3): (i) monoacetalization of the less hindered carbonyl group with 2,2-dimethylpropane-1,3-diol (**6**)→(**10**);[11] (ii) enolate formation of the free carbonyl group and trapping with trimethylsilyl chloride,[12] followed by bromination with NBS (**10**)→(**11**) (95% yield); and (iii) acid-catalysed hydrolysis of the acetal group (**11**) → (**7**) (81% yield).

When the bromo-diketone (**7**) was treated with strong bases, such as potassium t-butoxide, no definite products could be isolated. However, a weak base such as tetraethylammonium acetate did eliminate bromide, affording a crystalline compound that was purified by sublimation at high vacuum to give a waxy product of low melting point, in 96% yield. This product showed a single peak at g.l.c., the analytical and spectral data being in accordance with any of the two possible diketones (**8**) or (**9**).

Acetalization of the resulting cyclization product with 1 equiv. of 2,2-dimethylpropane-1,3-diol and chromatographic separation on silica gel gave three products, (**12**), (**13**), and (**14**), in a 133:23:10 ratio (total yield 78%). It was observed that whereas the major component (**12**) isomerises to product (**13**) under equilibrating acid conditions, the minor component (**14**) remains unchanged under the same conditions.

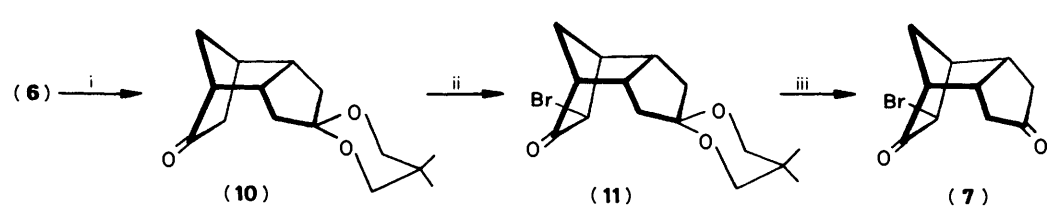
The analytical and spectral data of each of these three compounds were in agreement with those expected for a monoacetal of either (**8**) or (**9**). The presence of a third monoacetal clearly indicates that the cyclization product from the bromo diketone (**7**) is a mixture of the two possible diketones, one of them, however, predominating. That the third monoacetal is only present in minute amounts (6% of the total) accounts for the fact that the minor diketone was not spectroscopically detected in the crude cyclization product.

Although compounds (**8**) and (**9**) can both afford two different monoacetals, only those ones derived from (**8**) are specially suited to undergo an acid-catalysed transannular intramolecular transacetalization[13] from the kinetic monoacetal (the one from the enolisable carbonyl group) to the thermodynamic one (from the non-enolisable carbonyl group). The two functional groups in (**9**) are too far away, and linearly disposed, for interaction to occur.

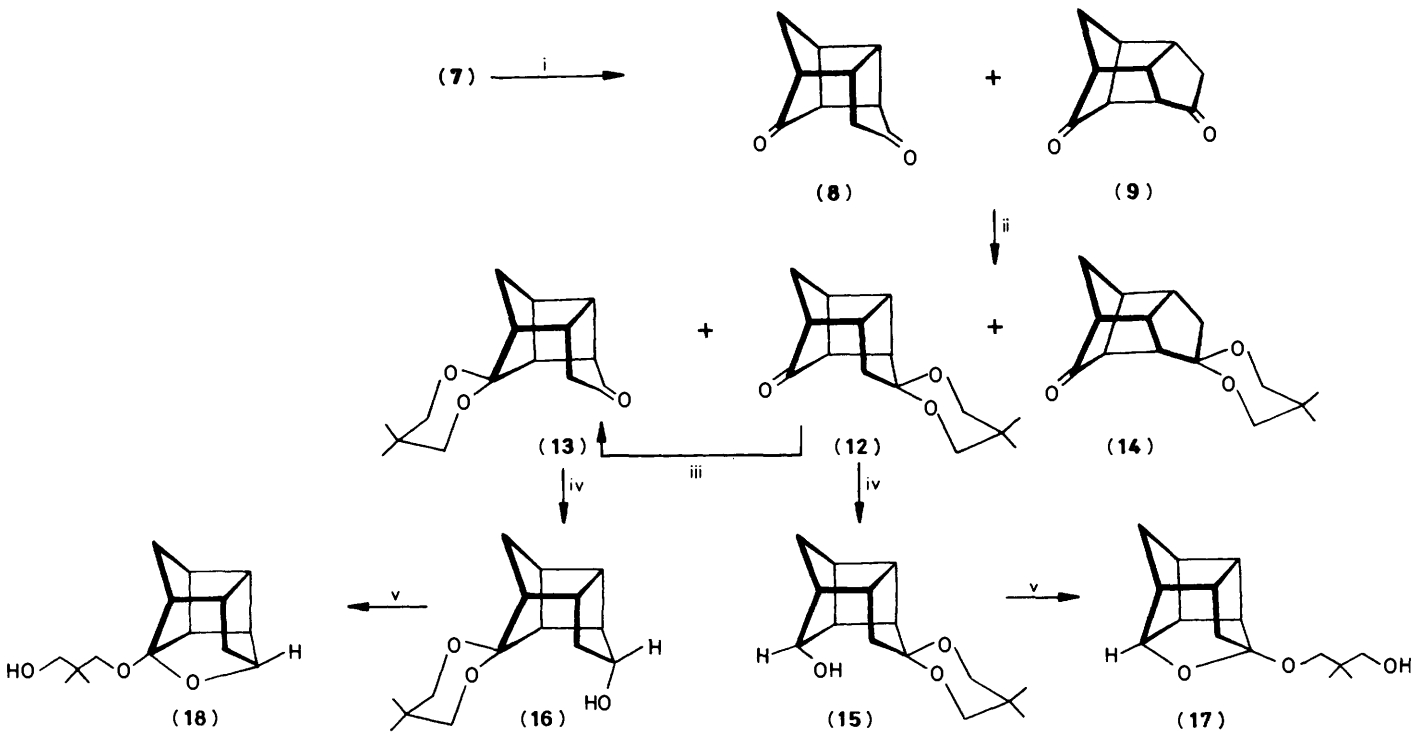
Accordingly (see Scheme 4), structure (**12**) must be assigned to the kinetic monoacetal of (**8**), structure (**13**) to the thermodynamic one, and structure (**14**) to the minor component. Further transannular interactions in monoacetals (**12**) and (**13**) could be dramatically demonstrated by $LiAlH_4$ reduction of the free carbonyl group. In both compounds the primarily formed secondary alcohols, (**15**) and (**16**) respectively, undergo an acid-catalysed rearrangement to give a pentacyclo derivative, (**17**) and (**18**), respectively, bearing a bridged acetal ether and a primary alcohol, as shown by ^1H n.m.r. spectroscopy, and confirmed either by preparation of the *p*-nitrobenzoate or by oxidation to the corresponding aldehyde. All the structural assignments, based on chemical methods, were confirmed either by *X*-ray diffraction analysis, for structures (**13**) and (**14**), or by two-dimensional n.m.r. spectroscopy for compound (**12**), as it is described below.

In order to gain some insight into the high regioselectivity observed in the intramolecular cyclization of the bromo diketone (**7**), some molecular mechanics calculations[14] on this compound and the diketones (**8**) and (**9**) were performed; the structures thus obtained are shown in Figure 1.

The greater facility of the enolate at position 3 to undergo



Scheme 3. i, 2,2-Dimethylpropane-1,3-diol/*p*-TsOH/C_6H_6; ii, $LiNPr^i{}_2$– Me_3SiCl, NBS; iii, Me_2CO/*p*-TsOH.



Scheme 4. i, $Et_4N^+AcO^-/Me_2CO$; ii, 2,2-dimethylpropane-1,3-diol–*p*-TsOH–C_6H_6; iii, *p*-TsOH–C_6H_6; iv, $LiAlH_4$–Et_2O; v, H^+

cyclization to afford the diketone (**8**), can be ascribed, on the one hand, to the greater proximity of positions 3 and 9 (3.0595 Å) compared with those of 5 and 9 (3.5448 Å), and on the other, owing to the stereo-electronic requirements of the reaction, to a better geometrical disposition of the enolate at position 3, in which the $2p_z$ orbital is almost completely collinear with the C–Br bond.

It is worth noting that, according to the molecular mechanics calculations, the predominant diketone (**8**) is *ca.* 91.88 kcal mol^{-1} less stable than the diketone (**9**), most of the high Pitzer strain of the former being ascribed to the angular tension created by the presence of the four-membered ring (see Table 1).

Table 1. Calculated values (in kcal mol^{-1}) for diketones (**8**) and (**9**) (MM2)[14]

	(8)	(9)
Heat of formation	55.67	−36.21
Total steric energy	149.21	57.34
Compression	10.73	1.82
Van der Waals	12.11	1.88
Bending	107.51	36.46
Stretch	−4.45	−1.36
Torsional	21.68	16.98
Dipole	1.64	1.57

It is well known that in the reductive ring-opening of a conjugated cyclopropyl ketone with lithium in liquid ammonia the bond that is cleaved is the one which overlaps better with the π system of the adjacent carbonyl group.[15] On the other hand, the reductive cleavage of C–C bonds which are not part of a cyclopropyl ring has only been observed if the corresponding bond is parallel to the π system of *two* adjacent carbonyl groups (or some other reducible functional groups). In this context, the monoacetal (**12**) appeared as an interesting substrate for a study of the possible reductive ring-opening of a cyclobutyl ketone. In practice, when the monoacetal (**12**) was treated with lithium in liquid ammonia only the starting tricyclic ketone acetal (**10**) was obtained. Accordingly, it is observed that, of the four C–C bonds in a position β to the carbonyl group, only the cyclobutane bond having maximum overlap with the π system of the carbonyl group is cleaved. To the best of our knowledge, this reaction represents the first example of a reductive ring-opening of a conjugated cyclobutyl ketone. The same stereo-electronic requirements observed in the reductive ring-opening of conjugated cyclopropyl ketones seem to apply here also. On

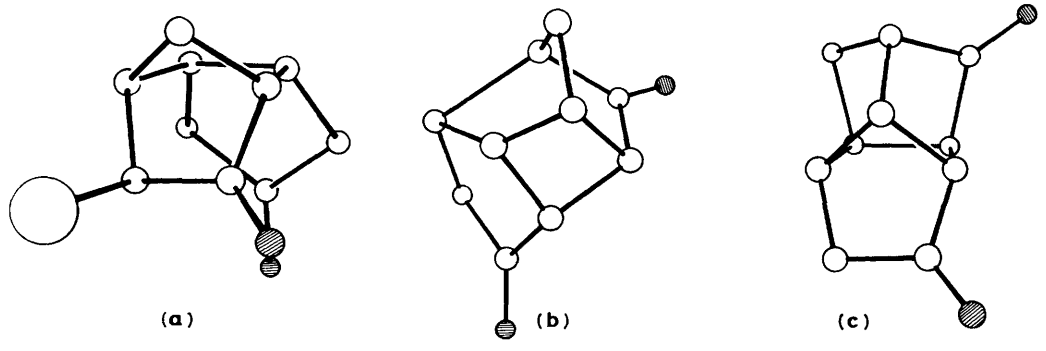


Figure 1. Drawings of the structures for compounds (**7**) (a), (**8**) (b), (**9**) (c) according to MM2 calculations

the other hand, reduction of the carbonyl group of the monoacetal (**14**) to a mixture of epimeric alcohols was the only reaction observed under the same reductive conditions (Li in liquid NH_3).

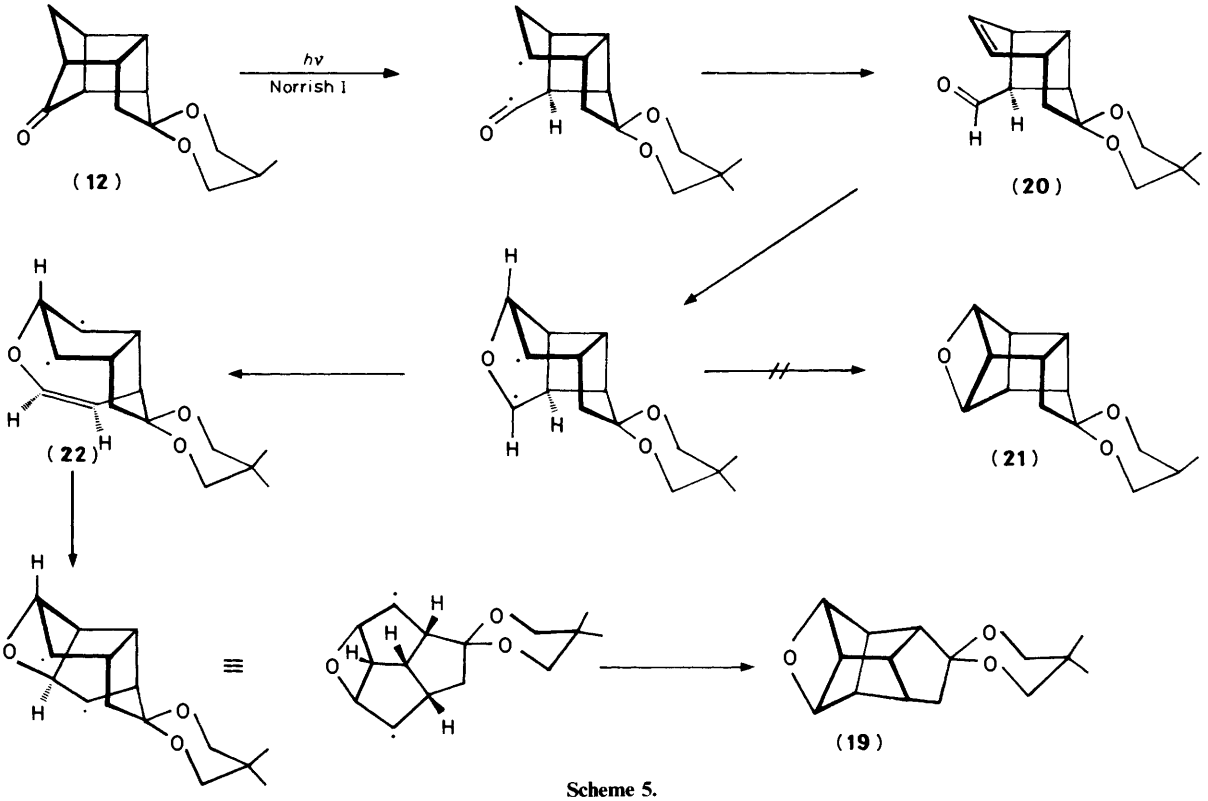
Since similar stereoelectronic requirements are also observed in the photochemical n→π* excitation of conjugated cyclopropyl ketones, which usually leads to β homolytic cleavage,[16] the photochemistry of the monoacetal (**12**) was also investigated in order to see how far the behaviour of a conjugated cyclobutyl ketone parallels that of a conjugated cyclopropyl homologue.

Irradiation of a solution of the monoacetal (**12**) in benzene–t-butyl alcohol (4:1), in a quartz tube, by means of a Hanau lamp, operating at 500 W, leads to the oxetane (**19**) in 20—40% yields, together with variable amounts of an isomeric unsaturated aldehyde (**20**) (17—26%), depending upon the irradiation time (7—15 h) (see Scheme 5).

Since it is well known[18] that the Paterno-Buchi reaction, far from being a concerted process, proceeds *via* a 1,4-diradical species, it is probable that the observed rearrangement takes place in this step: *i.e.*, it could proceed *via* the olefin diradical (**22**). It is worth noting that the formation of this intermediate from the diradical generated in the first step of the Paterno-Buchi reaction would imply the rearrangement of a cyclobutylcarbinyl radical into a bis-homoallyl radical. In fact, formation of products derived from the rearrangement of a cyclopropylcarbinyl radical into a homoallyl radical has been considered as proof of the presence of 1,4-diradical species in Paterno-Buchi cycloadditions.[19]

Structural Assignments

N.m.r. Spectroscopic Data.—The structures of compounds (**8**) and (**12**)—(**15**), as well as those of (**17**) and (**19**) were



Scheme 5.

Whereas the structure of the oxetane (**19**) could be determined by *X*-ray diffraction analysis (see below), the instability of the unsaturated aldehyde (**20**) did not allow an unequivocal structural assignment and it could only be studied by the routine spectroscopic methods (i.r., ^1H n.m.r., m.s.), the proposed structure being only a tentative one.

It is generally accepted[17] that photochemical formation of oxetanes from ketones proceeds *via* a Norrish type I cleavage affording as a primary photochemical product an acyl-alkyl radical which, by proton transfer, would lead to an unsaturated aldehyde suitable for use in an intramolecular Paterno-Buchi cycloaddition. However, such a sequence of reactions, starting from the monoacetal (**12**) did not lead to the oxetane (**19**) with the skeleton of (**5**). We must conclude, therefore, that rearrangement occurred at some stage of the reaction, probably as a result of the high strain inherent in the unrearranged oxetane (**21**), which with two four-membered rings, is *ca.* 90 kcal mol^{-1} less stable than (**19**), as estimated from MM calculations.

confirmed by detailed analysis of their 200 MHz ^1H n.m.r. spectra, with the aid of selective decoupling experiments (see experimental part and Figure 2 for the numbering of the skeletons).

In the case of structures (**8**), (**12**), and (**19**) auto-correlated 2D homonuclear ^1H n.m.r. experiments were also performed. For

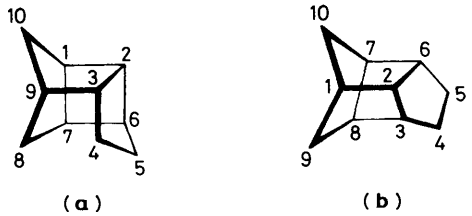


Figure 2. Position numbering systems used in the formal naming and in description of n.m.r. spectra: (a) tetracyclo[5.3.0.$0^{2,6}$.$0^{3,9}$]decane; (b) tetracyclo[5.2.1.$0^{2,6}$.$0^{3,8}$]decane

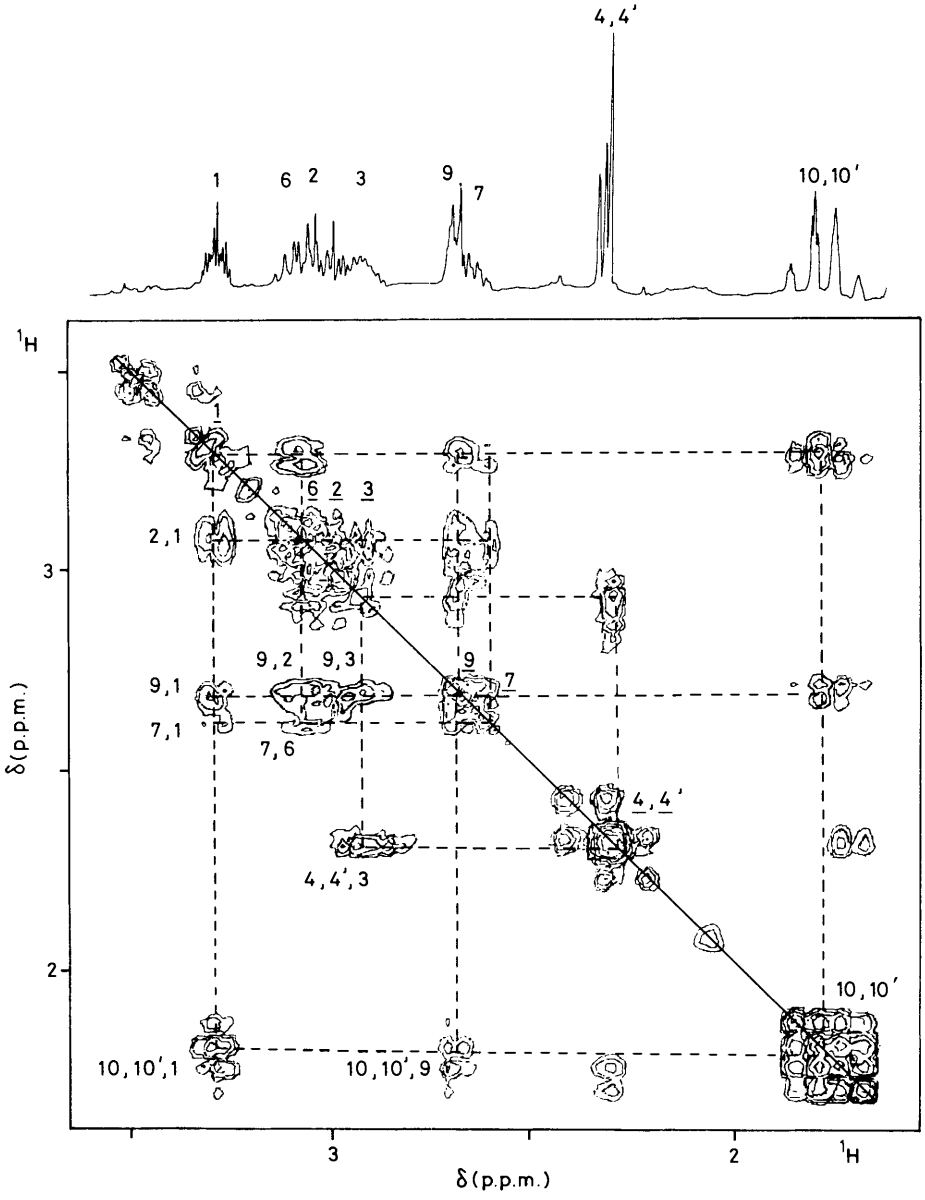


Figure 3. Contour plot of an auto-correlated 2D homonuclear ^{1}H n.m.r. experiment (aliphatic region) for compound (8)

compounds (**8**) (Figure 3) and (**12**) (Figure 4), in addition to the signals along the diagonal corresponding to the conventional one-dimentional spectrum, the off-diagonal signals show all the expected vicinal couplings except the H_2-H_3 and H_2-H_6 for (**8**) and H_1-H_2, H_2-H_6, and H_3-H_9 for (**12**), that must be masked by the signals on the diagonal due to the proximity of chemical shift.

Additional off-diagonal signals are assigned to W couplings: H_1-H_9 and H_2-H_9 for compound (**8**) and H_1-H_9, H_3-H_6, and H_7-H_9 for compound (**12**). Molecular models analysis shows that the same W couplings are expected for both compounds, but the non-observed couplings H_3-H_6 and H_7-H_9 for compound (**8**) and H_2-H_9 for (**12**) cannot be distinguished probably because the proximity of chemical shift mentioned before.

The ^{1}H n.m.r. spectrum for structure (**19**) shows a well resolved series of multiplets so that in the auto-correlated 2D homonuclear ^{1}H n.m.r. experiment (Figure 5) all the vicinal couplings are present together with five W couplings: H_2-H_7, H_2-H_8, H_1-H_7, H_1-H_8, and H_6-H_3.

Since structure (**19**) has been determined by *X*-ray diffraction analysis, the pairs of dihedral angles involved in all possible W couplings show that only those in which the coupling is observed, are the values for the angles in the range 165—180°, in all the other cases the angles being far from these values.

Since structure (**12**) could not be determined by *X*-ray diffraction analysis owing to the lack of adequate crystals, additional 2D n.m.r. experiments[20] were performed in order to confirm as far as possible the structure assigned to it.

Once ^{1}H n.m.r. spectra were assigned according to the above experiments, a proton-carbon chemical shift correlation[21] (Figure 6) allowed us to make the assignment of the ^{13}C n.m.r. spectra, which is in agreement with the result of a RELAY experiment[22] ($J_{C,H}$ 125 Hz, $J_{H,H}$ 6 Hz) (Figure 7) that establishes the following concordance connections: C_1–C_2, C_3–C_9, C_6–C_7.

X-Ray Diffraction Analysis.—As stated above, the structure of compounds (**13**), (**14**), and (**19**) have been determined by *X*-ray diffraction analysis and a brief discussion of the most salient structural details of these compounds follows.

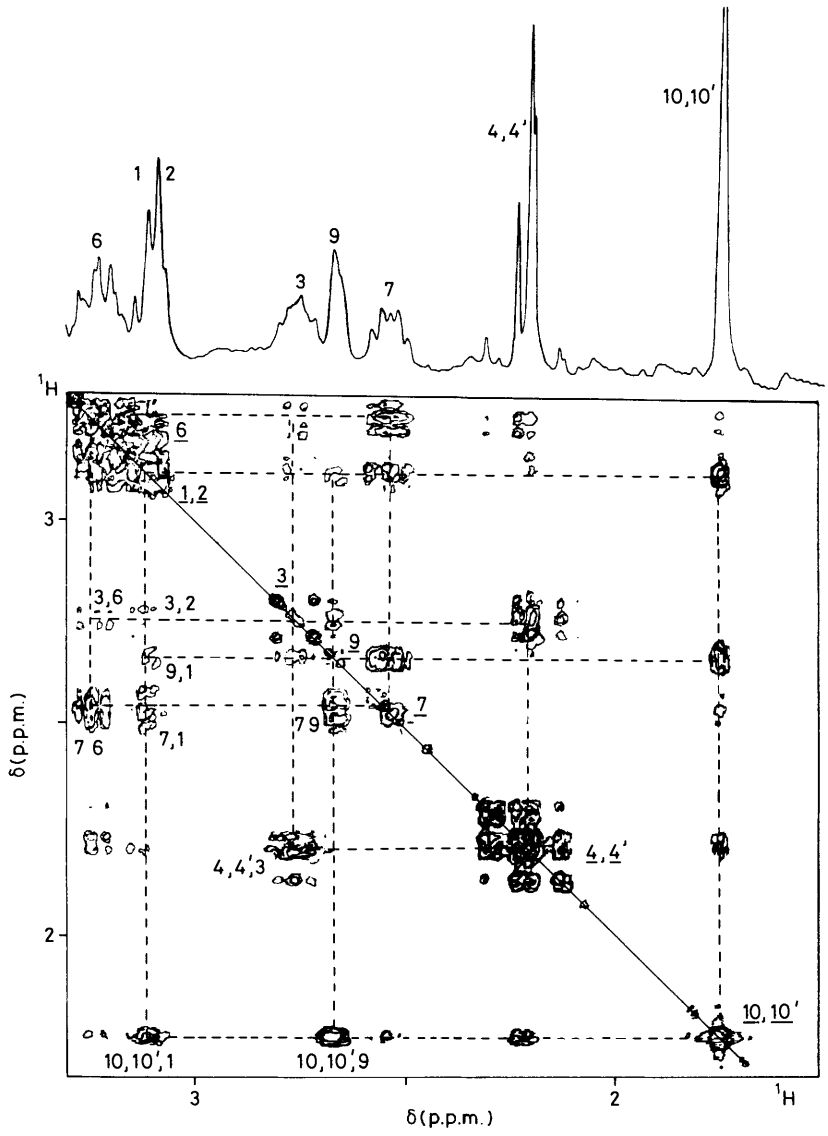


Figure 4. Contour plot of an auto-correlated 2D homonuclear ^{1}H n.m.r. experiment (aliphatic region, δ = 1.5—3 p.p.m.) for compound (**12**)

Table 2. Fractional atomic co-ordinates ($\times 10^4$) for non-hydrogen atoms for compound (**13**) with e.s.d.s in parentheses

	Atom	*x*	*y*	*z*		Atom	*x*	*y*	*z*
Molecule A:	O(1)	5 351(1)	2 951(2)	8 667(2)	Molecule B:	O(1)	357(1)	2 956(2)	4 957(2)
	C(2)	5 295(2)	3 433(3)	10 213(2)		C(2)	313(2)	3 344(3)	3 675(3)
	C(3)	4 766(2)	2 445(3)	10 924(3)		C(3)	−232(2)	2 297(3)	2 317(3)
	C(4)	5 457(3)	1 620(3)	10 558(4)		C(4)	427(3)	1 430(4)	2 228(3)
	O(5)	5 502(2)	1 206(2)	8 981(2)		O(5)	517(2)	1 157(2)	3 592(2)
	C(6)	5 958(2)	2 142(3)	8 329(3)		C(6)	991(2)	2 168(2)	4 822(3)
	C(7)	7 257(2)	2 678(3)	8 703(3)		C(7)	2 283(2)	2 745(2)	4 779(3)
	C(8)	7 690(3)	1 895(4)	7 374(4)		C(8)	2 788(2)	2 078(3)	5 652(3)
	C(9)	6 667(4)	846(4)	6 547(5)		C(9)	1 801(2)	1 039(3)	5 848(4)
	C(10)	5 865(2)	1 594(3)	6 649(3)		C(10)	970(2)	1 752(3)	6 202(3)
	C(11)	6 543(3)	2 558(4)	5 946(3)		C(11)	1 650(2)	2 794(3)	7 526(3)
	C(12)	7 786(3)	2 872(4)	6 626(4)		C(12)	2 874(2)	3 120(2)	7 025(3)
	C(13)	7 777(2)	3 780(3)	8 197(3)		C(13)	2 789(2)	3 908(2)	6 061(3)
	C(14)	7 010(3)	4 443(3)	7 813(3)		C(14)	2 031(2)	4 587(3)	6 772(3)
	O(14)	7 011(2)	5 409(2)	8 573(3)		C(15)	1 373(2)	3 953(3)	7 852(3)
	C(15)	6 319(3)	3 740(3)	6 338(3)		C(16)	−107(3)	2 730(4)	944(4)
	C(16)	4 866(3)	2 975(4)	12 607(3)		C(17)	−1 481(2)	1 714(3)	2 503(4)
	C(17)	3 521(3)	1 814(4)	10 317(4)					

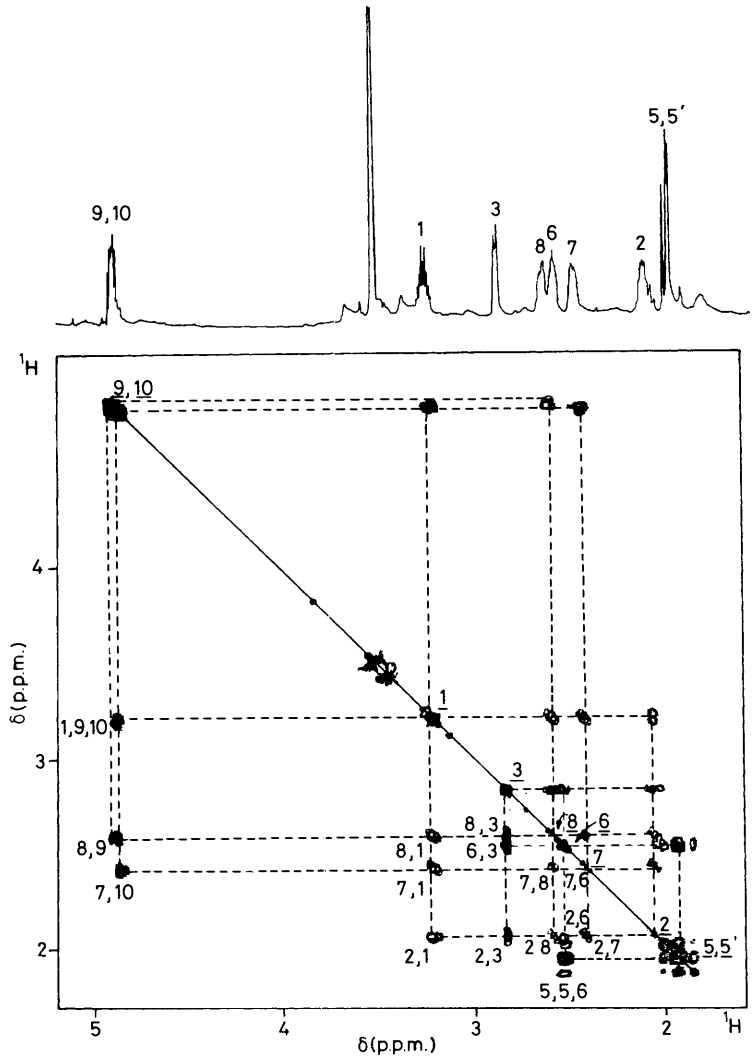


Figure 5. Contour plot of an auto-correlated 2D homonuclear ^{1}H n.m.r. experiment (aliphatic region δ = 1.5—5 p.p.m.) for compound (**19**)

Table 3. Selected bond distances and angles for compound (**13**) with e.s.d.s in parentheses

Distances (Å)	Molecule A	Molecule B	Angles (°)	Molecule A	Molecule B
C(6)–C(7)	1.542(4)	1.548(3)	C(6)–C(10)–C(9)	100.9(3)	99.9(2)
C(6)–C(10)	1.544(4)	1.525(4)	C(12)–C(11)–C(15)	104.5(3)	104.4(2)
C(7)–C(8)	1.586(5)	1.566(5)	C(7)–C(6)–C(10)	101.4(2)	101.2(2)
C(7)–C(13)	1.574(5)	1.562(3)	C(6)–C(7)–C(8)	101.6(2)	101.8(2)
C(8)–C(9)	1.527(5)	1.528(4)	C(6)–C(7)–C(13)	111.6(3)	111.7(2)
C(8)–C(12)	1.533(7)	1.548(4)	C(8)–C(7)–C(13)	89.4(2)	89.3(2)
C(9)–C(10)	1.533(7)	1.548(5)	C(7)–C(8)–C(9)	108.0(3)	107.2(2)
C(10)–C(11)	1.542(5)	1.548(3)	C(7)–C(8)–C(12)	86.1(3)	86.2(2)
C(11)–C(12)	1.563(5)	1.562(4)	C(9)–C(8)–C(12)	105.7(4)	105.1(2)
C(11)–C(15)	1.529(6)	1.537(5)	C(8)–C(9)–C(10)	94.3(3)	94.7(3)
C(12)–C(13)	1.546(4)	1.529(5)	C(9)–C(10)–C(11)	101.0(3)	101.3(2)
C(13)–C(14)	1.508(6)	1.524(4)	C(10)–C(11)–C(12)	102.6(3)	102.1(2)
C(14)–O(14)	1.224(5)	1.206(4)	C(8)–C(12)–C(13)	92.4(3)	91.2(2)
C(14)–C(15)	1.523(4)	1.529(4)	C(11)–C(12)–C(13)	100.3(3)	100.5(2)
			C(8)–C(12)–C(11)	102.9(3)	103.4(2)
			C(10)–C(11)–C(15)	118.4(3)	118.3(3)
			C(6)–C(10)–C(11)	108.8(2)	110.3(2)

In the asymmetric unit of structures (**13**) and (**14**) two independent molecules are observed. The differences in bond angles or lengths are not significant and may be ascribed to packing forces.

Whereas most of the C–C bond distances in structure (**13**) (see Figure 8 and Table 3) are in the range of standard values, 1.53 ± 0.02 Å, two of the bonds of the cyclobutane ring are longer than those values: A 1.586(5), B 1.566(5) Å and A

Table 4. Fractional atomic co-ordinates ($\times 10^4$) for non-hydrogen atoms for compound (**14**) with e.s.d.s in parentheses

	Atom	*x*	*y*	*z*		Atom	*x*	*y*	*z*
Molecule A:	O(1)A	1 254(2)	2 773(4)	7 285(4)	Molecule B:	O(1)	6 223(2)	2 421(3)	4 119(4)
	C(2)	1 822(4)	3 076(7)	6 821(7)		C(2)	6 787(3)	2 324(7)	5 175(6)
	C(3)	2 504(4)	2 974(6)	7 826(6)		C(3)	7 473(3)	2 550(6)	4 862(5)
	C(4)	2 523(4)	1 803(6)	8 377(8)		C(4)	7 399(3)	3 685(6)	4 202(6)
	O(5)	1 913(2)	1 549(4)	8 758(4)		O(5)	6 782(2)	3 732(3)	3 180(3)
	C(6)	−413(4)	1 369(7)	8 347(7)		C(6)	4 500(3)	3 376(6)	1 199(6)
	O(6)	−746(3)	1 887(5)	8 925(6)		O(6)	4 234(2)	2 758(4)	350(5)
	C(7)	4(4)	1 811(7)	7 484(7)		C(7)	4 891(3)	3 094(6)	2 521(6)
	C(8)	−104(4)	837(7)	6 492(8)		C(8)	4 685(3)	4 110(5)	3 273(5)
	C(9)	−624(5)	29(2)	6 885(8)		C(9)	4 163(4)	4 766(6)	2 257(6)
	C(10)	−248(4)	134(7)	8 289(7)		C(10)	4 588(4)	4 649(5)	1 299(6)
	C(11)	552(4)	208(6)	8 299(7)		C(11)	5 351(3)	4 750(5)	2 110(5)
	C(12)	558(4)	120(6)	6 932(6)		C(12)	5 301(3)	4 921(5)	3 450(5)
	C(13)	1 211(5)	717(7)	6 817(8)		C(13)	5 965(3)	4 462(6)	4 316(6)
	C(14)	1 299(3)	1 668(6)	7 792(6)		C(14)	6 164(3)	3 498(5)	3 540(5)
	C(15)	701(4)	1 499(6)	8 363(7)		C(15)	5 590(3)	3 512(5)	2 355(5)
	C(16)	3 092(5)	3 127(8)	7 252(9)		C(16)	8 056(4)	2 601(10)	6 030(6)
	C(17)	2 538(5)	3 876(8)	8 841(9)		C(17)	7 601(4)	1 604(7)	4 004(7)

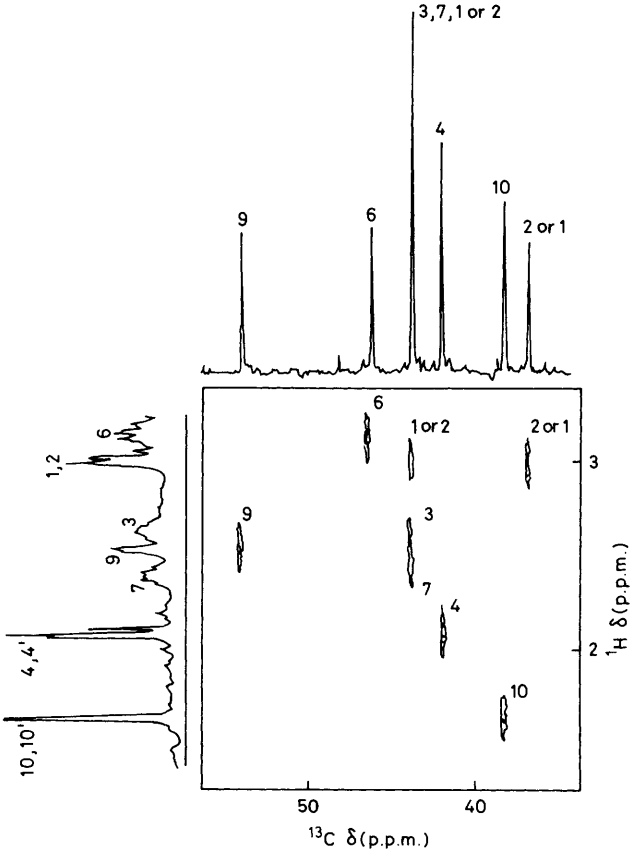


Figure 6. Contour plot of a proton-carbon chemical shift correlation experiment (aliphatic region, ^{1}H δ = 1.5—3 p.p.m., ^{13}C δ = 35—55 p.p.m.) for compound (**12**)

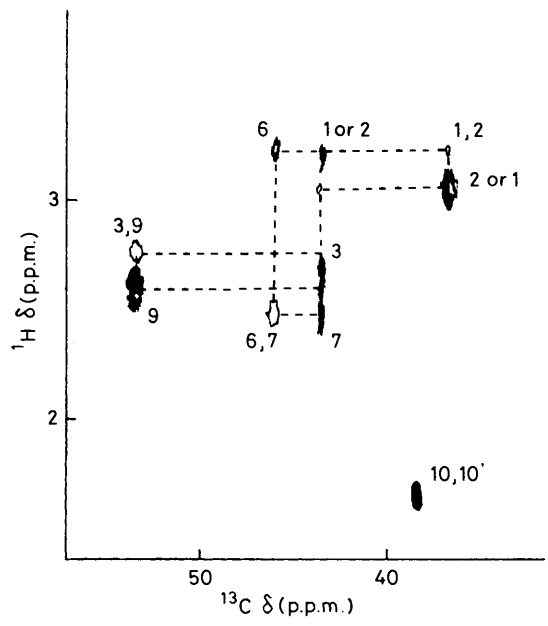


Figure 7. Contour plot of a RELAY experiment ($J_{C,H}$ = 125 Hz, $J_{H,H}$ = 6 Hz) for compound (**12**)

1.574(5), B 1.562(3) Å for C(7)–C(8) and C(7)–C(13), respectively.

On the other hand, strain in structure (**13**) is clear from the C–C–C angles; in fact, besides the values near 90° for those of the cyclobutane ring [A 89.4(2), B 89.3(2)°, A 86.1(3), B 86.2(2)°, A 92.4(3), B 91.2(2)° and A 86.1(2), B 87.0(2)° for C(7), C(8), C(12), C(13)], there are other angles which are also smaller than the standard values [A 94.3(3), B 94.7(3)° for C(8)–C(9)–C(10)]. The distortion of the structure is also evident from the conformation of the three five-membered rings C(6),C(7),C(8),-C(9),C(10), C(8),C(9),C(10),C(11),C(12), and C(11),C(12),-C(13),C(14),C(15), which have 'skew envelope' conformations, so that taking C(10), C(9), and C(11) as the atoms out of the plane, the four remaining atoms of the five-membered rings show torsion angles of A −11.5°, B 11.0°; A 10.6°, B −11.1°; A 15.0°, B −16.5°.

Bonds C(7)–C(8) and C(10)–C(11), in structure (**14**) (see Figure 9 and Table 5), with distances of A 1.576(11), B 1.584(9) Å and A 1.606(12), B 1.570(8) Å, which are also longer than the standard values, produce a shortening of all the angles of the eight-membered ring defined by C(6),C(7),C(15),C(11),C(12),-C(8),C(9),C(10), the smaller values corresponding to the angles

Table 5. Selected bond distances and angles for compound (**14**) with e.s.d.s in parentheses

Distances (Å)	Molecule A	Molecule B	Angles (°)	Molecule A	Molecule B
C(6)–O(6)	1.212(11)	1.208(8)	C(7)–C(6)–C(10)	98.2(7)	97.3(5)
C(6)–C(7)	1.525(12)	1.518(8)	C(6)–C(7)–C(8)	101.3(6)	102.0(5)
C(6)–C(10)	1.505(11)	1.519(9)	C(8)–C(7)–C(15)	102.1(6)	101.0(5)
C(7)–C(8)	1.576(11)	1.584(9)	C(7)–C(8)–C(9)	103.3(6)	102.4(5)
C(7)–C(15)	1.531(9)	1.546(9)	C(7)–C(8)–C(12)	103.3(7)	103.3(5)
C(8)–C(9)	1.563(13)	1.541(8)	C(8)–C(9)–C(10)	92.8(6)	94.1(5)
C(8)–C(12)	1.545(11)	1.538(9)	C(6)–C(10)–C(11)	100.3(6)	101.2(5)
C(9)–C(10)	1.559(11)	1.541(11)	C(6)–C(10)–C(9)	93.8(3)	93.8(5)
C(10)–C(11)	1.606(12)	1.570(8)	C(9)–C(10)–C(11)	103.5(7)	103.1(5)
C(11)–C(12)	1.535(11)	1.540(9)	C(10)–C(11)–C(12)	104.9(6)	105.6(5)
C(15)–C(11)	1.558(10)	1.544(8)	C(10)–C(11)–C(15)	103.5(6)	104.0(5)
C(12)–C(13)	1.525(12)	1.529(8)	C(8)–C(12)–C(11)	92.9(6)	92.7(4)
C(14)–C(13)	1.546(11)	1.548(9)	C(11)–C(12)–C(13)	106.5(6)	107.5(5)
C(14)–C(15)	1.514(11)	1.513(7)	C(12)–C(13)–C(14)	102.8(7)	102.6(5)
			C(13)–C(14)–C(15)	104.1(6)	103.5(5)
			C(7)–C(15)–C(11)	94.3(5)	94.4(5)
			C(11)–C(15)–C(14)	106.0(6)	107.2(4)
			C(10)–C(6)–O(6)	132.7(6)	132.7(6)

Table 6. Fractional atomic co-ordinates ($\times 10^4$) for non-hydrogen atoms for compound (**19**) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
O(1)	4 264(3)	2 187(3)	2 983(3)
C(2)	3 869(5)	1 598(6)	1 749(6)
C(3)	4 110(4)	2 470(5)	598(5)
C(4)	5 339(5)	2 777(6)	813(6)
O(5)	5 629(3)	3 378(3)	2 072(3)
C(6)	5 944(6)	3 222(7)	6 698(6)
C(7)	5 362(5)	2 421(6)	5 542(5)
C(8)	6 190(5)	1 202(6)	5 636(6)
C(9)	6 938(5)	1 714(6)	6 815(6)
C(10)	7 100(5)	3 116(6)	6 228(5)
O(10)	6 233(4)	2 238(4)	7 735(4)
C(11)	6 940(4)	2 978(5)	4 728(5)
C(12)	6 849(5)	1 457(5)	4 498(5)
C(13)	6 176(5)	1 251(5)	3 180(5)
C(14)	5 400(4)	2 488(5)	3 097(5)
C(15)	5 700(5)	3 206(5)	4 359(6)
C(16)	3 863(6)	1 674(7)	−649(6)
C(17)	3 432(5)	3 752(6)	535(7)

Table 7. Selected bond distances and angles for compound (**19**) with e.s.d.s in parentheses

Distance (Å)		Angles (°)	
C(6)–C(7)	1.550(8)	C(10)–C(6)–C(7)	95.1(4)
C(6)–C(10)	1.542(8)	C(8)–C(7)–C(6)	95.9(4)
C(6)–O(10)	1.469(7)	C(15)–C(7)–C(8)	102.6(4)
C(7)–C(8)	1.577(8)	C(9)–C(8)–C(7)	97.1(4)
C(7)–C(15)	1.541(7)	C(10)–C(9)–C(8)	94.4(4)
C(8)–C(9)	1.537(7)	O(10)–C(9)–C(10)	92.3(4)
C(8)–C(12)	1.510(7)	C(9)–C(10)–C(6)	77.4(4)
C(9)–C(10)	1.542(8)	C(11)–C(10)–C(6)	106.9(4)
C(9)–O(10)	1.442(7)	C(11)–C(10)–C(9)	107.8(4)
C(10)–C(11)	1.549(7)	C(9)–O(10)–C(6)	82.9(4)
C(11)–C(12)	1.534(7)	C(12)–C(11)–C(10)	104.0(4)
C(11)–C(15)	1.543(7)	C(15)–C(11)–C(10)	105.0(4)
C(12)–C(13)	1.535(7)	C(15)–C(11)–C(12)	93.0(4)
C(13)–C(14)	1.551(7)	C(11)–C(12)–C(8)	94.6(4)
C(14)–C(15)	1.501(7)	C(13)–C(12)–C(11)	107.1(4)
		C(14)–C(13)–C(12)	102.4(4)
		C(15)–C(14)–C(13)	103.5(4)
		C(11)–C(15)–C(7)	93.6(4)
		C(14)–C(15)–C(11)	107.2(4)

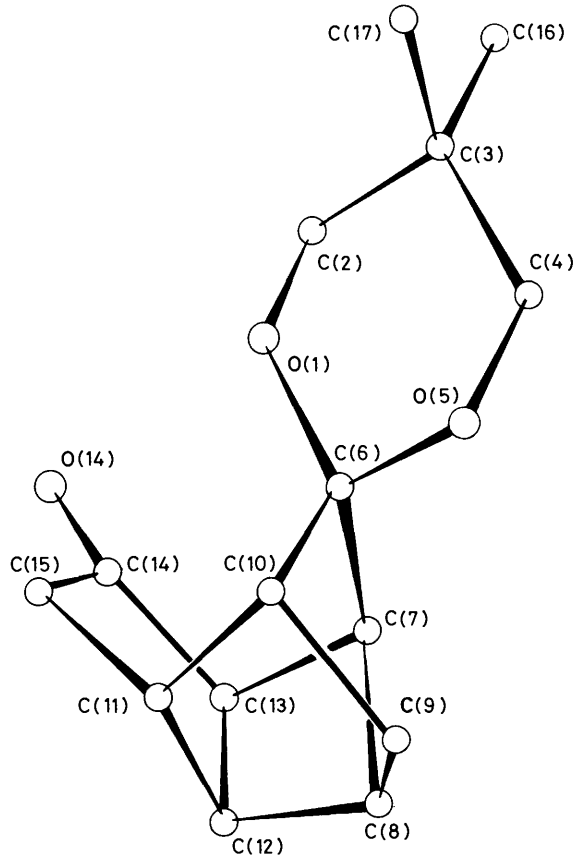


Figure 8. Perspective view of compound (**13**)

C(7)–C(15)–C(11) [A 94.3(5), B 94.4(5)°], C(11)–C(12)–C(8) [A 92.9(6), B 92.7(4)°] and C(8)–C(9)–C(10) [A 92.8(6)–B 94.1(5)°], and a value of A 98.2(7), B 97.3(5)° for C(10)–C(6)–C(7) which is really small for a C–CO–C angle. With such a structure, the conformations of all five-membered rings are practically perfect 'envelopes'.

In structure (**19**) (see Figure 10 and Table 7), which has a similar carbon skeleton to that of compound (**14**), whilst the C(7)–C(8) bond is very long [1.577(8) Å], the presence of the

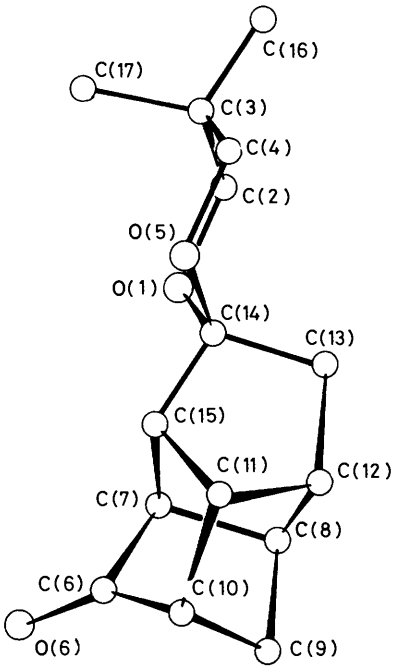


Figure 9. Perspective view of compound (**14**)

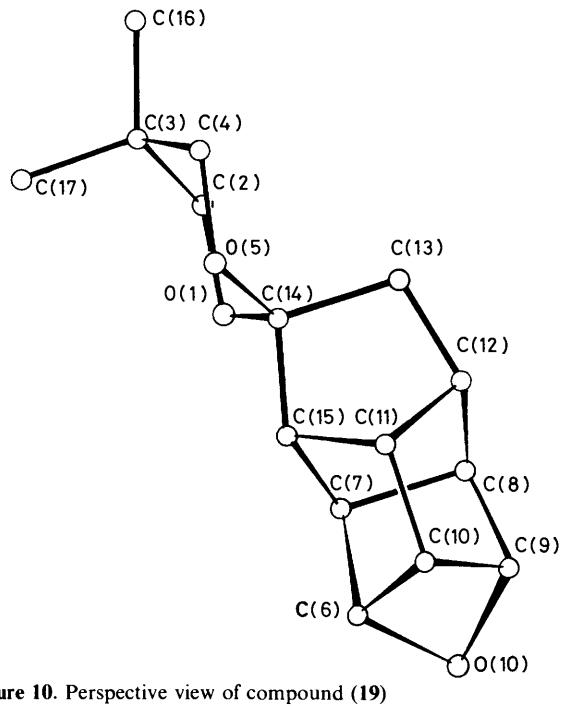


Figure 10. Perspective view of compound (**19**)

ether bridge pulls the C(10) atom so that the C(10)–C(11) bond is now smaller [1.549(7) Å]. With regard to the bond angles of *ca.* 94° mentioned above in structure (**14**) the C(6)–C(7)–C(8) and C(7)–C(8)–C(9) angles also have small values [95.9(4)° and 97.1(4)°, respectively]. Such a feature modifies the conformation of rings C(6),C(7),C(15),C(11),C(10) and C(10),C(11),C(12),-C(8),C(9) which are now 'skew envelopes', so that taking C(7) and C(8) as the atoms out of the plane, they show torsion angles of 7.6° and −7.6° respectively.

Experimental

M.p.s were taken on a Buchi capillary melting point apparatus and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer Model 681 spectrophotometer. ^{1}H N.m.r. at 60 MHz were recorded on a Perkin-Elmer Model R-24 spectrometer, and those at 200 MHz and carbon-13 magnetic resonance on a Varian XL-200. The mass spectra were recorded in a Hewlett-Packard 5930A spectrometer, and g.l.c. analyses were run on a Hewlett-Packard 5790A gas chromatograph, using 1/8 in × 2 m metallic columns filled with 3% SE-30 on Chromosorb W. Ether refers to diethyl ether.

exo-9-*Bromo*-5′,5′-*dimethyltricyclo*[5.2.1.0^{2,6}]*decane*-4-*spiro*-2′-(1′,3′-*dioxan*)-8-*one* (**11**).—Di-isopropylamine (4.8 ml, 37 mmol) in anhydrous tetrahydrofuran (THF, 30 ml) was added under a dry nitrogen atmosphere to a stirred mixture of butyl-lithium in hexane (1.6M; 23 ml, 37 mmol) and THF (30 ml) cooled in an ice-bath. The mixture was stirred for 5 min, after which the monoacetal (**10**) (4.71 g, 1.9 mmol) dissolved in anhydrous THF (60 ml) was added. The cooling bath was then removed and the reaction mixture stirred for 1 h at room temperature. The mixture was cooled once again and tri-methylsilyl chloride (7 ml) added; the mixture was then stirred for 15 min at room temperature and finally poured into cooled, saturated aqueous $NaHCO_3$ and extracted with ether. The combined ether extracts were dried ($MgSO_4$) and evaporated under reduced pressure to afford the enol silyl ether as a yellow solid (8.69 g); δ_H(60 MHz; $CDCl_3$) 0.15 (9 H, s), 1.0 (6 H, s), 1.3 (13 H, complex m), 3.4 (2 H, s), 3.6 (2 H, s), and 4.7 (1 H, d, *J* 2.8 Hz).

(b) A solution of the crude enol silyl ether (8.9 g, 19 mmol), in anhydrous THF (60 ml), was cooled in an ice bath and a solution of *N*-bromosuccinimide (3.7 g, 20 mmol) in anhydrous THF was added, during 30 min. The reaction mixture was then poured into saturated aqueous $NaHCO_3$, extracted with ether, and the combined ether extracts dried ($MgSO_4$) and evaporated under reduced pressure to give a white solid (8.1 g). This was chromatographed on silica gel (150 g) with 10% hexane–ethyl acetate as eluant to afford the *title compound* (**11**) (5.92 g, 95%), m.p. 134—136 °C (Found: C, 54.7; H, 6.45. $C_{15}H_{21}BrO_3$ requires C, 54.72; H, 6.44%); $\nu_{max.}$($CHCl_3$) 2 960, 2 880, 1 754, and 1 112 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 0.85 (3 H, s), 1.0 (3 H, s), 1.3 (12 H, complex m), 3.3 (2 H, s), 3.4 (2 H, s), and 4.2 (1 H, d, *J* 3.6 Hz); *m/z*, 328—330 (6%, M^+), 249 (60), 245—243 (6), 181 (11), 167 (67), and 128 (100).

exo-9-*Bromotricyclo*[5.2.1.0^{2,6}]*decane*-4,8-*dione* (**7**).—To a solution of the bromoacetal (**11**) (1.2 g) in anhydrous acetone (60 ml), a few crystals of toluene-*p*-sulphonic acid were added and the mixture stirred for 4 days at room temperature. It was then treated with K_2CO_3 (0.30 g) and stirred for 10 min after which the solid material was filtered off and the filtrate evaporated. The resulting residue was dissolved in CH_2Cl_2 and the solution washed with saturated aqueous $NaHCO_3$, dried ($MgSO_4$), and evaporated, and the residue chromatographed on silica gel (50 g) and eluted with hexane–ethyl acetate; the 40% fraction afforded the title compound (**7**) as a white solid (0.72 g, 81%), m.p. 87 °C (from pentane–CCl_4); $\nu_{max.}$(KBr) 1 740 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 2.0 (2 H, m), 2.4 (4 H, m), 3.0 (4 H, m), and 3.85 (1 H, d, *J* 4 Hz); *m/z* 242—244 (12%, M^+), 163 (17), 135 (47), 91 (70), and 53 (100).

Intramolecular Cyclization of the 9-*Bromo Diketone* (**7**) *induced by Tetraethylammonium Acetate: the Tetracyclodiones* (**8**) *and* (**9**).—Tetraethylammonium acetate (4 g) was added to a solution of the 9-bromo diketone (**7**) (2.0 g, 8.2 mmol) in anhydrous acetone (50 ml), and the mixture was stirred for 20 min at room temperature. Precipitated tetraethylammonium bromide was filtered off, the filtrate evaporated, and the residue

dissolved in CH_2Cl_2; the solution was then washed with saturated aqueous $NaHCO_3$, and dried ($MgSO_4$). Evaporation of the solution gave a solid which upon sublimation at 130 °C/0.5 Torr gave *tetracyclo*[5.3.0.0^{2,6}.0^{3,9}]*decane-5,8-dione* (**8**) as a waxy white solid (1.28 g, 96.4%; one peak on g.l.c.) contaminated with minor amounts of tetracyclo-[5.2.1.0^{2,6}.0^{3,8}]decane-4,9-dione (**9**) (see below) (Found: C, 73.35; H, 6.3. $C_{10}H_{10}O_2$ requires C, 74.05; H, 6.21%); $\nu_{max.}$($CHCl_3$) 2 960, 2 950, 2 880, 1 750, and 1 740 cm^{-1}; δ_H (200 MHz; $CDCl_3$) 1.80 (10-H, one half of an AB pattern, $J_{10,10'}$ 12 Hz, $J_{10,9}$ 1 Hz, $J_{10,1}$ 1.6 Hz), 1.91 (10'-H, one half of an AB pattern, $J_{10,10'}$ 12 Hz, $J_{10',9}$ 1.2 Hz, $J_{10',1}$ 1.6 Hz), 2.42 (4-H, 4'-H, m), 2.75 (9-H, 2-H, m), 3.05 (3-H, 6-H, 7-H, m), and 3.40 (1-H, t of q, $J_{1,2} = J_{1,7}$ 4.4 Hz, $J_{1,10} = J_{1,10'} = J_{1,9}$ 1.6 Hz); δ_C (50 MHz; $CDCl_3$) 37.2 (t), 38.3 (d), 41.0 (d), 41.4 (d), 42.9 (t), 46.6 (d), 51.6 (d), 54.0 (d), 213.3 (s), and 215.7 (s); *m/z* 162 (M^+, 5%), 133 (2), 105 (4), 97 (11), 91 (30), and 66 (100).

Monoacetglization of the Tetracyclodiones (**8**) *and* (**9**): *5',5'-Dimethyltetracyclo*[5.3.0.0^{2,6}.0^{3,9}]*decane-5-spiro-2'-(1',3'-dioxan)-8-one* (**12**), *5',5'-Dimethyltetracyclo-*[5.3.0.0^{2,6}.0^{3,9}]*decane-8-spiro-2'-(1',3'-dioxan)-5-one* (**13**), *and 5',5'-Dimethyltetracyclo*[5.2.1.0^{2,6}.0^{3,8}]*decane-4-spiro-2'-(1',3'-dioxan)-9-one* (**14**).—2,2-Dimethylpropane-1,3-diol (0.309 g, 2.0 mmol) and a few crystals of toluene-*p*-sulphonic acid were added to a solution of the above crude tetracyclodiones (0.437 g, 2.7 mmol) in benzene (100 ml), and the mixture heated for 24 h under a Dean-Stark trap. The mixture was then washed with saturated aqueous $NaHCO_3$, dried ($MgSO_4$), and evaporated under reduced pressure to give a crude mixture of monoacetals which was chromatographed on silica gel (Merck, 230—400 mesh; 30 g). Elution with hexane–ethyl acetate (10 and 15%) gave the title monoacetals (**12**) (0.42 g), (**13**) (0.08 g), and (**14**) (0.03 g), in 78% overall yield.

Compound (**12**), m.p. 83—85 °C (from pentane–CH_2Cl_2) (Found: C, 72.15; H, 8.2. $C_{15}H_{20}O_3$ requires C, 72.55; H, 8.12%); $\nu_{max.}$($CHCl_3$) 2 965, 2 880, 1 750, 1 120, and 1 100 cm^{-1}; δ_H (200 MHz; $CDCl_3$) 0.87 (3 H, s), 0.96 (3 H, s), 1.70 (10-H, 10'-H, br s), 2.18 and 2.24 (4-H, 4'-H, AB pattern, $J_{4,4'}$ 13 Hz, $J_{4,3}$ 3 Hz, $J_{4',3}$ 6 Hz), 2.54 (7-H, m), 2.67 (9-H, m), 2.74 (3-H, m), 3.10 (1-H, 2-H, m), 3.20 (6-H, m), 3.32 and 3.36 (2 H, AB pattern, J_{AB} 12 Hz), and 3.43 and 3.45 (2 H, AB pattern, J_{AB} 12 Hz); δ_C (50 MHz; $CDCl_3$) 22.2 (q), 22.4 (q), 29.8 (s), 36.2 (d), 37.8 (t), 41.5 (t), 43.5 (d), 43.6 (d), 43.8 (d), 46.6 (d), 54.6 (d), 71.8 (t), 72.7 (t), 110.7 (s), and 214.5 (s); *m/z* 248 (M^+, 9%), 220 (3), 193 (10), 154 (11), and 128 (100).

Compound (**13**), m.p. 75 °C (Found: C, 72.45; H, 8.1. $C_{15}H_{20}O_3$ requires C, 72.55; H, 8.12%); $\nu_{max.}$(CCl_4) 2 960, 2 860, 1 740, 1 115, 1 095, 1 085, 1 050, and 1 030 cm^{-1}; δ_H (200 MHz; $CDCl_3$) 0.78 (3 H, s), 1.08 (3 H, s), 1.44 (10-H, one half of an AB pattern, $J_{10,10'}$ 11 Hz, $J_{10,1} = J_{10,9}$ 1.2 Hz), 1.95 (10'-H, one half of an AB pattern, $J_{10,10'}$ 11 Hz, $J_{10',1} = J_{10',9}$ 1.2 Hz), 2.14 (4-H, one half of an AB pattern, $J_{4,4'}$ 18 Hz, $J_{4,3}$ 7.6 Hz), 2.55 (1 H, 1-H or 9-H, m), 2.70 (1 H, m), 2.78 (4'-H, one half of an AB pattern, $J_{4',4}$ 18 Hz, $J_{4',3}$ 0 Hz), 2.8 (2 H, 7-H, m), 2.94 (1 H, 1-H or 9-H, m), 3.15 (1 H, m), 3.20 and 3.28 [2 H, AB pattern, J_{AB} 12 Hz, J_{BD} 1.8 Hz (W)], and 3.38 and 3.47 [2 H, CD pattern, J_{CD} 12 Hz, J_{BD} 1.8 Hz (W)]; δ_C (50 MHz; $CDCl_3$) 22.2 (q), 27.7 (q), 28.8 (s), 36.1 (t), 37.7 (d), 41.2 (d), 41.6 (d), 42.2 (d), 42.9 (t), 46.7 (d), 46.8 (d), 70.2 (t), 72.0 (t), 107.3 (s), and 219.2 (s); *m/z* 248 (M^+, 30%), 220 (4), 168 (22), and 154 (100).

Compound (**14**), m.p. 106—108 °C (Found: C, 72.6; H, 8.1. $C_{15}H_{20}O_3$ requires C, 72.55; H, 8.12%); $\nu_{max.}$(CCl_4) 2 960, 2 850, 1 770, 1 130, and 1 100 cm^{-1}; δ_H (200 MHz; $CDCl_3$) 0.91 (3 H, s), 0.98 (3 H, s), 1.72 (10-H, 10'-H, m), 1.92 and 2.03 (5-H, 5'-H, AB pattern, $J_{5,5'}$ 14 Hz, $J_{5,6}$ 0 Hz, $J_{5',6}$ 5 Hz), 2.26 (4 H, m), 2.60 (2 H, m), 3.39 and 3.42 (2 H, AB pattern, J_{AB} 14 Hz), 3.48 (2 H, s); δ_C (50 MHz; $CDCl_3$) 22.2 (q), 22.5 (q), 29.9 (s), 37.6 (t), 38.8 (d), 39.6 (t), 43.0 (d), 43.4 (d), 43.7 (d), 47.5 (d), 51.2 (d), 71.23 (t), 72.59 (t), 104.9 (s), 211.2 (s); *m/z* 248 (M^+, 3%), 220 (50), 154 (20), and 128 (100).

Acid-catalysed Intramolecular Transacetalization of (**12**) *to* (**13**).—A solution of the monoacetal (**12**) (0.182 g) in benzene (13 ml) and a few crystals of toluene-*p*-sulphonic acid were heated under reflux for 48 h. The solution was then washed with saturated aqueous $NaHCO_3$, dried ($MgSO_4$), and evaporated to afford, quantitatively crystalline compound (**13**), m.p. 75 °C, identical in all respects with authentic material.

$LiAlH_4$ *Reduction of* 8-*Oxotetracycloacetal* (**12**)/*Acid-catalysed Rearrangement: 5',5'-Dimethyltetracyclo-*[5.3.0.0^{2,6}.0^{3,9}]*decane-5-spiro-2'-(1',3'-dioxan)-8-ol* (**15**) *and* 10-(3-*Hydroxy*-2,2-*dimethylpropoxy*)-9-*oxapentacyclo-*[5.4.0.0^{2,5}.0^{3,10}.0^{4,8}]*undecane* (**17**), *and Its* p-*Nitrobenzoate Derivative.*—(*a*) $LiAlH_4$ (0.080 g, 2 mmol) in anhydrous ether (15 ml) under a nitrogen atmosphere was cooled in an ice bath whilst a solution of the monoacetal (**12**) (0.250 g, 1 mmol) in anhydrous ether (10 ml) was added dropwise with stirring; the latter was then continued at room temperature for 2 h. The reaction mixture was then cooled again with an ice-bath, diluted with CH_2Cl_2 (50 ml) and hydrolysed with saturated aqueous sodium potassium tartrate, the excess of water being eliminated with Na_2SO_4. The inorganic salts were filtered off and solvent removed to give compound (**15**) (0.250 g) as oily material; $\nu_{max.}$(NaCl) 3 420, 2 980, 2 880, 1 120, and 1 100 cm^{-1}; δ_H (200 MHz; $CDCl_3$) 0.94 (3 H, s), 0.98 (3 H, s), 1.25 (10-H, one half of an AB pattern, $J_{10,10'}$ 11 Hz, $J_{10,9} = J_{10,1}$ 1 Hz), 1.45 (10'-H, one half of an AB pattern, $J_{10,10'}$ 11 Hz, $J_{10',9} = J_{10',1}$ 1 Hz), 2.16 (4-H, one half of an AB pattern, $J_{4,4'}$ 14.5 Hz, $J_{4,3}$ 8.4 Hz), 2.29 (1 H, m), 2.3—2.8 (5 H, m), 2.73 (4'-H, one half of an AB pattern, $J_{4,4'}$ 14.5 Hz, $J_{4',3}$ 0 Hz), 2.90 (1 H, m), 3.49 (4 H, m), 3.80 (8-H, dd of t, $J_{8,OH}$ 9 Hz, $J_{8,7}$ 6 Hz, $J_{8,9} = J_{8,3}$ 1 Hz), and 5.56 (OH, d, $J_{OH,8}$ 9 Hz).

(*b*) Acid-catalysed rearrangement, either spontaneously in the n.m.r. tube for 12 h or by addition of 'aged' $CDCl_3$, gave a further oily product to which the structure of the bridged acetal derivative (**17**) was assigned; it showed the following spectroscopic properties: $\nu_{max.}$(NaCl) 3 450, 2 950, 2 880, 1 105, 1 050, and 1 020 cm^{-1}; δ_H (200 MHz; $CDCl_3$) 0.85 (3 H, s), 0.86 (3 H, s), 1.30 (10-H, one half of an AB pattern, $J_{10,10'}$ 10.8 Hz, $J_{10,9} = J_{10,1}$ 1.6 Hz), 1.40 (10'-H, one half of an AB pattern, $J_{10',10}$ 10.8 Hz, $J_{10',9} = J_{10',1}$ 1.6 Hz), 1.82 (4-H, one half of an AB pattern, $J_{4,4'}$ 11.2 Hz, $J_{4,3}$ 4 Hz), 2.14 (4'-H, one half of an AB pattern, $J_{4',4}$ 11.2 Hz, $J_{4',3}$ 0 Hz), 2.25 (1 H, m), 2.5—2.8 (6 H, complex m), 3.27 and 3.38 (2 H, AB pattern, J_{AB} 9.6 Hz), 3.27 and 3.47 (2 H, AB pattern, J_{AB} 11.2 Hz), 4.77 (8-H, m); δ_C($CDCl_3$) 21.7 (q), 21.8 (q), 34.7 (d), 36.2 (s), 37.0 (t), 39.5 (t), 40.2 (d), 44.0 (d), 44.04 (d), 45.2 (d), 45.6 (d), 69.1 (t), 71.4 (t), 85.2 (d), and 115.6 (s); *m/z* 250 (10%, M^+), 233 (12), 222 (4), 207 (3), 205 (3), 193 (6), 165 (14), 164 (13), 141 (8), 128 (26), and 43 (100).

(*c*) The *p*-nitrobenzoate (79% yield), prepared from the rearranged alcohol (**17**) (0.100 g, 0.4 mmol) and *p*-nitrobenzoyl chloride (0.110 g, 0.6 mmol) in pyridine (10 ml) had m.p. 65 °C; $\nu_{max.}$($CHCl_3$) 1 725, 1 530, and 1 275 cm^{-1}; δ_H (200 MHz; $CDCl_3$) 1.08 (6 H, s), 1.25 (10-H, one half of an AB pattern, $J_{10,10'}$ 10.8 Hz, $J_{10,9} = J_{10,1}$ 1.6 Hz), 1.32 (10'-H, one half of an AB pattern, $J_{10',10}$ 10.8 Hz, $J_{10',9} = J_{10',1}$ 1.6 Hz), 1.67 (4-H, one half of an AB pattern, $J_{4',4}$ 11.2 Hz, $J_{4,3}$ 4 Hz), 2.00 (4'-H, one half of an AB pattern, $J_{4',4}$ 11.2 Hz, $J_{4',3}$ 0 Hz), 2.10 (1 H, m), 2.3—2.7 (6 H, complex m), 3.30 and 3.50 (2 H, AB pattern, J_{AB} 9.6 Hz), 4.00 (2 H, s), 4.50 (8-H, m), and 7.88 (4 H, m); δ_C (50 MHz; $CDCl_3$) 22.01 (q), 34.69 (d), 35.29 (s), 37.06 (t), 39.40 (t), 40.26 (d), 43.90 (d), 45.59 (d), 70.33 (t), 71.15 (t), 82.68 (d), 115.04 (s), 123.53 (2 × d), 130.65 (2 × d), 136.02 (s), 150.61 (s), and 164.61 (s); *m/z* 399 (M^+, 5%), 314 (2), 236 (62), 181 (16), 164 (25), 150 (100), 104 (52), and 69 (87).

$LiAlH_4$ *Reduction of Compound* (**13**)*/Acid-catalysed Rearrangement: 5′,5′-Dimethyltetracyclo*[5.3.0.0^{2,6}.0^{3,9}]*decane-8-spiro-2′*(1′,3′*-dioxan*)*-5-ol* (**16**) *and* 8*-(3-Hydroxy-2,2-dimethyl)-propoxy-9-oxapentacyclo*[5.4.0.0.0^{2,5}.0^{3,10}.0^{4,8}]*undecane* (**18**).—Starting from the monoacetal (**13**), and in a similar experiment to that described for the monoacetal (**12**), the title compounds (**16**) and (**18**) were obtained in quantitative yields.

Compound (**16**), $\nu_{max.}$(KBr) 3 450, 2 960, 2 940, 2 880, 1 100, and 1 090 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 0.8 (3 H, s), 1.2 (3 H, s), 1.3—3.0 (10 H, complex m), 3.1 (4 H, m), and 4.0 (1 H, m).

Compound (**18**) (Found: C, 71.75, H, 8.7. $C_{15}H_{22}O_3$ requires C, 71.96 H, 8.85%); $\nu_{max.}$(NaCl) 3 450, 2 960, 2 860, 1 100, 1 090, and 1 050 cm^{-1}; δ_H (200 MHz; $CDCl_3$) 0.86 (3 H, s), 0.87 (3 H, s), 1.34 (10-H, 10′-H, m), 1.77 and 2.01 (4-H, 4′-H, AB pattern, $J_{4,4'}$ 12.8 Hz), 2.28 (1 H, m), 2.4—2.7 (3 H, m), 2.82 (1 H, m), 2.94 (1 H, m), 3.35 and 3.38 (2 H, AB pattern, J_{AB} 10.4 Hz), 3.32 and 3.44 (2 H, AB pattern, J_{AB} 9.6 Hz), and 4.46 (5-H, m).

Oxidation of Compound (**17**) *to the Corresponding Aldehyde*.—A solution of the primary alcohol (**17**) (0.090 g, 0.36 mmol) in CH_2Cl_2 (5 ml) was added dropwise to a stirred solution of pyridinium chlorochromate (PCC) (0.125 g, 0.57 mmol) in CH_2Cl_2 (10 ml) and the mixture stirred at room temperature for 5 h. Ether was added and the mixture passed through a column of silica gel (3 g), with ether (100 ml). The eluant was evaporated to give the aldehyde as a colourless oil (0.070 g, 79%); $\nu_{max.}$(NaCl) 2 960, 2 860, 2 700, and 1 730 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 1.1 (s, 6 H), 1.3 (2 H, m), 1.4—3 (11 H, complex m), 3.45 (2 H, m), 4.7 (1 H, m), and 9.4 (1 H, s); δ_C (50 MHz; $CDCl_3$) 18.99 (2 × q), 34.60 (d), 37.04 (t), 39.34 (t), 40.24 (d), 43.88 (2 × d), 45.44 (d), 45.54 (d), 69.63 (t), 85.46 (d), 114.98 (s), and 205.57 (s); *m/z* 249 (M^+ + H, 0.4%), 177 (0.4), 165 (13), 164 (9), 147 (5), 117 (11), 105 (15), 91 (25), 79 (17), 66 (50), and 41 (100).

Li/NH_3 *Reduction of Compound* (**12**) *to 5′,5′-Dimethyltricyclo*[5.2.1.0^{2,6}]*decane-4-spiro-2′-*(1′,3′*-dioxan*)*-8-one* (**10**).—Lithium (0.040 g, 5.7 mmol) was added with stirring to liquid NH_3 (50 ml) under anhydrous conditions to give a deep blue solution. The monoacetal (**12**) (0.150 g, 6 mmol) in anhydrous ether (15 ml) was then added dropwise followed by further additions of lithium in order to keep the deep blue colour of the solution for a 40 min period. The ammonia was then allowed to evaporate after which the residue was diluted with water (50 ml) and ether (100 ml). The aqueous layer was saturated with NaCl, extracted with ether (3 × 50 ml) and the combined ether extracts washed with saturated brine, dried ($MgSO_4$), and evaporated under reduced pressure. The resulting residue was chromatographed on silica gel (Merck, 230—400 mesh; 10 g): elution with mixtures of hexane–ethyl acetate gave starting material (0.033 g) and a white crystalline compound (0.055 g) identical in all respects with an authentic sample of the tricyclic monoacetal (**10**).

$Li/Liquid\ NH_3$ *Reduction of the 9-Oxotetracycloacetal* (**14**).—Starting from the monoacetal (**14**) (0.080 g) and employing the reaction conditions described above, a heavy oil (0.060 g) was obtained which was characterised as a 60:40 mixture of the two epimers of the corresponding 9-hydroxy derivative: $\nu_{max.}$(NaCl) 3 450, 2 960, 2 880, and 1 110 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 0.8 (s, 3 H, 40%), 0.9 (s, 3 H, 60%), 0.92 (s, 3 H, 60%), 1.0 (s, 3 H, 40%), 1.1—2.5 (complex m, 12 H), 3.38 (m, 5 H), and 3.95 (m, 1 H); *m/z* 250 (M^+, 36%), 233 (6), 193 (12), 167 (15), 164 (16), 154 (16), 141 (20), and 128 (100).

Photolysis of the 8*-Oxotetracycloacetal* (**12**): *5′,5′-Dimethyl-2-oxapentacyclo*[6.2.1.0^{3,10}.0^{4,11}.0^{5,9}]*undecane-7-spiro-2′-*(1′,3′*-dioxane*) (**19**).—In an iced-water refrigerated quartz tube a solution of the 8-oxotetracycloacetal (**12**) (0.135 g, 5.4 mmol), in anhydrous benzene (16 ml), containing anhydrous t-butyl alcohol (6 ml), under an N_2 atmosphere was irradiated with a 500 W Hanau lamp. The photochemical reaction was monitored by g.l.c. (initial temperature 140 °C, gradient 10 °C min^{-1} and a flux of 30 ml min^{-1}) and showed after 7 h, the presence of only two peaks (R_t 6.32 and 7.31 min) in a 41:59 relative ratio. Elimination of solvents afforded a crude oil (0.140 g) which was chromatographed on silica gel (Merck, 230—400 mesh; 10g); elution with hexane–ethyl acetate mixtures of increasing polarity gave two products: (i) a colourless oil (0.035 g, 26%), the same R_t (6.32) observed in the analytical control, to which the structure of the unsaturated aldehyde (**20**) is tentatively assigned; $\nu_{max.}$(NaCl) 2 960, 2 830, 2 720, 1 720, and 1 110 cm^{-1}; δ_H (60 MHz; $CDCl_3$) 0.75 (3 H, s), 1.0 (3 H, s), 1—3.3 (7 H, complex m), 3.2 (2 H, s), 3.4 (2 H, s), 5.75 (2 H, q, *J* 6 Hz), and 9.75 (1 H, s); *m/z* 248 (M^+, 6%), 220 (4), 192 (7), 162 (12), 128 (72), 91 (45), and 69 (100). (ii) A white solid (0.030 g, 22%), m.p. 88—89 °C (from pentane), with the same R_t (7.31) as the other component detected in control analysis by g.l.c., to which the structure of the title compound (**19**) was assigned by spectroscopic techniques and confirmed by *X*-ray diffraction analysis (Found: C, 72.45; H, 8.2. $C_{15}H_{20}O_3$ requires C, 72.55; H, 8.12%); $\nu_{max.}$(CCl_4) 2 990, 2 950, 2 860, and 1 110 cm^{1}; δ_H (200 MHz; $CDCl_3$) 0.93 (3 H, s), 1.01 (3 H, s), 1.87 and 1.93 (5-H, 5′-H, AB pattern, $J_{5,5'}$ 13 Hz, $J_{5,6}$ 1.6 Hz, $J_{5',6}$ 4.8 Hz), 2.04 (2-H, m), 2.40 (7-H, m), 2.52 (6-H, m), 2.58 (8-H, m), 2.80 (3-H, m), 3.20 (1-H, q of t, $J_{1,10} = J_{1,9} = J_{1,2}$ 4 Hz, $J_{1,7} = J_{1,8}$ 1.6 Hz), 3.47 (2 H, s), 3.48 (2 H, s), and 4.86 (9-H, 10-H, m); δ_C (50 MHz; $CDCl_3$) 22.4 (2 × q), 30.0 (s), 36.9 (t), 41.8 (d), 45.2 (d), 46.3 (d), 49.9 (d), 55.7 (d), 57.4 (d), 71.1 (t), 72.9 (t), 91.8 (d), 91.9 (d), and 106.8 (s); *m/z* 248 (M^+, 7%), 219 (12), 183 (29), 179 (17), 154 (17), 128 (40), and 69 (100). In a further run, under the same conditions, starting from the monoacetal (**12**) (0.250 g, 1 mmol) and increasing the reaction time up to 15 h, the analytical g.l.c. control (same conditions) of aliquots showed the following ratios:

	Reaction time (h)				
R_t (min)	2	5	7	11	15
6.31	71	60	48	36	28
7.31	29	40	52	64	72

Elimination of solvent after 15 h irradiation, afforded a mixture of starting material (0.070 g) together with polymeric material from the aldehyde (**20**), and the bridged acetal (**19**) (0.100 g, 40%).

X-Ray Diffraction Analyses of Compounds (**13**), (**14**), *and* (**19**).—*Crystal data.* Compound (**13**): $C_{15}H_{20}O_3$, F_w = 268.5, triclinic, a = 12.471(3), b = 12.404(3), c = 9.474(2) Å, α = 105.34(2), β = 90.36(2), γ = 108.48(3), V = 1 333.9(9) Å^3, $P\bar{1}$, D_x = 1.34 g cm^{-3}, Z = 4. Compound (**14**): $C_{15}H_{20}O_3$, F_w = 268.5, monoclinic, a = 20.090(4), b = 11.850(2), c = 11.178(2) Å, β = 105.14(2), V = 2 569(1) Å^3, $P2_1/c$, D_x = 1.39 g cm^{-3}, Z = 8. Compound (**19**): $C_{15}H_{20}O_3$, F_w = 268.5, monoclinic, a = 12.225(2), b = 9.946(1), c = 10.335(2) Å, β = 95.59(2), V = 1 250.6(5) Å^3, $P2_1/a$, D_x = 1.43 g cm^{-3}, Z = 4.

Cell-parameters determination and intensity measurements. A similar process was used for all three compounds in which a small colourless crystal was mounted on a Philips PW-1100 four-circle diffractometer. Cell-parameters were determined from 25 reflections ($6 \leqslant \theta \leqslant 9$), the orientation matrix being refined by least-squares. Intensities were collected with Mo-K_α radiation, monochromatised by reflection from a graphite crystal; the ω-scan technique was used with a scan width of

1° and scan speed of 0.03° s^{-1}. 4 170 Reflections for compound (**13**), 2 308 for (**14**) and 895 for (**19**) were collected in the range $2 \leqslant \theta \leqslant X$, where $X = 30°$, 22.5°, and 24.5°, respectively: 4 040, 2 268, and 860 of these which were assumed as observed applying the condition $I \geqslant 2.5\ \sigma(I)$. Lorentz-polarisation corrections were made.

Crystal structure determination and refinement. The three structures were determined by direct methods, using the MULTAN system of computer programs.[23] Fourier maps computed from the set of phases with the highest combined figure of merit revealed the position of non-hydrogen atoms. Only in structure (**19**) was there a need to correct the origin position with the TRADIR method of DIRDIF system of computer programs.[24] Isotropic and anisotropic refinements by full-matrix least-squares method were carried out with the SHELX76 computer program.[25] The function minimised was $w(F_o - F_c)^2$, where $w = [\sigma^2(F_o) + k\,(F_o)^2]^{-1}$, being $k = 0.038$ (**13**), 0.043 (**14**), and 0.014 (**19**). f, f' and f'' were from 'International Tables of Crystallography.'[26] A difference synthesis revealed the position of 32 (**13**), 40 (**14**), and 19 H atoms (**19**), which were refined with an overall isotropic temperature factor; the rest were calculated. Final R values were 0.088, 0.084, and 0.047, respectively ($R_w = 0.094$, 0.093, and 0.053). Non-significant features have been observed on the final difference Fourier map.

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