Di-isophorone and Related Compounds. Part 26.[1] Reactions of Bicyclo[4.2.1]nonane-7-spiro-2'-(tetrahydrofuran) Derivatives

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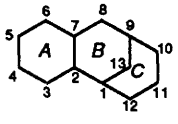
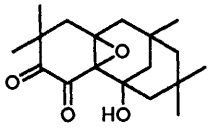
A number of interconversions of compounds of the bicyclo[4.2.1]nonane-7-spiro-2'-(tetrahydrofuran) ring system, comprising reduction, oxidation, and Grignard reactions, confirm the structural and conformational stability of this carbon skeleton. Representative compounds undergo scission under electron impact according to a common fragmentation pattern.

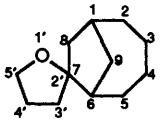
We have recently described[2] a rearrangement of the tricyclo[7.3.1.0^{2,7}]tridecane (**A**) to the bicyclo[4.2.1]nonane-7-spiro-2'-(tetrahydrofuran) ring system (**C**), which occurs when 1-hydroxy-2,7-epoxydi-isophorane-3,4-dione (**B**)[3] is oxidised with hydrogen peroxide in acidic media. The resulting keto acid (**1**) of the new spirane ring system (**C**) arises by a multi-stage process consisting essentially of a Baeyer–Villiger oxidation, a recyclisation, and a pinacol rearrangement. Since the mechanism of this transformation involves all the functional groups of the reactant (**B**), the observed reaction (**B**) ⟶ (**1**) is, so far, its only known example, but the keto acid (**1**) serves as a versatile source of related compounds of the same skeletal structure.[2] A number of further interconversions now described confirm the structural and conformational stability of the new ring system. The rupture under electron impact of representative compounds is explicable in terms of a common fragmentation pattern, consolidating the structural evidence.



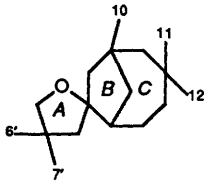
(**A**)



(**B**)



(**C**)



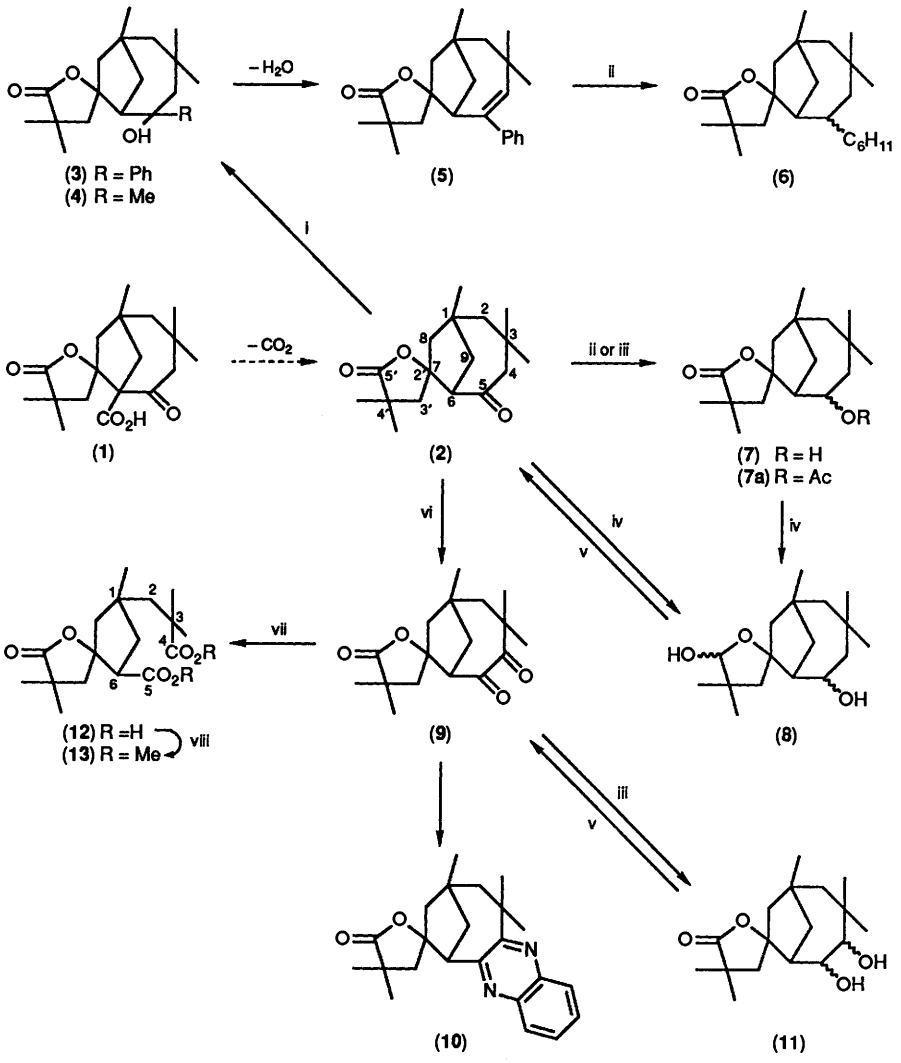
(**D**)

The central starting material of the present interconversions was the neutral keto lactone (**2**), which is readily accessible from the primary rearrangement product (**1**) by decarboxylation.[2] Reduction by lithium aluminium hydride, affecting both its lactone and ring ketone groups, gave the 5,5'-diol (**8**), the two intense γ-lactone and ring-carbonyl IR bands[2] of substrate (**2**) giving way, in the product (**8**), to a broad hydroxy peak centred at 3 290 cm^{-1}. The intermediate hydroxy lactone (**7**), previously obtained from keto lactone (**2**) by catalytic hydrogenation,[2] was produced more conveniently by the use of sodium borohydride.[4] Like compound (**2**), it yielded the 5,5'-diol (**8**) on further lithium aluminium hydride reduction. The maintainance of both structure and conformation of the ring skeleton is shown by the reconversion, in high yield, of the 5,5'-diol (**8**) into the original keto lactone (**2**) by Kiliani oxidation.[5] Lithium aluminium hydride normally reduces lactones with simultaneous ring cleavage directly to the linear diol, terminating only rarely at the intermediate cyclic secondary alcohol stage.[6] Amongst substituted γ-butyrolactones, for example, 4,4-dimethyl-3,3-diphenyltetrahydrofuran-2-one yields the 2-hydroxytetrahydrofuran or 2,2-dimethyl-3,3-diphenylbutane-1,4-diol under mild or more severe conditions, respectively.[7] The preservation of the furan ring in the present reductions exemplifies the less common course of the reaction.

The conversion of ketones into 1,2-dicarbonyl compounds by oxidation with selenium dioxide is a well documented reaction[3,8] that has been widely applied to alicyclic structures, including steroids and triterpenes, as well as a diisophorone derivative (**B**)[3]. Extended to the spiro-compound (**2**), the oxidation gave fair yields of a yellow product, $C_{17}H_{24}O_4$, formulated as the α-diketone (**9**) on the basis of its origin and properties. Its IR spectrum retains the characteristic γ-lactone carbonyl band[9a] (at 1 770 cm^{-1}) and displays a strong peak (at 1 700 cm^{-1}) in the range of alicyclic 1,2-diketones,[9b,10] *i.e.* at a slightly higher frequency than the parent monoketone (by 15 cm^{-1}).[3,9b,11] Its failure to absorb significantly in the near-UV range is ascribed to its inability to enolise to the corresponding hydroxy ketone,[12] the anti-Bredt structure of which is disfavoured. The selenium dioxide oxidation of cycloheptanone, the prototype of the present example, has been described previously;[13] it is clearly not inhibited by the presence of a *gem*-dimethyl group adjacent to the oxidation site, or by the seven-membered ketone being part of a bridged bicyclic structure. The stability of the γ-lactone moiety of the spirane structure (**9**) under the drastic conditions of the oxidation is noteworthy.

The chemical behaviour of compound (**9**) confirmed its α-diketone structure: on treatment with *o*-phenylenediamine, it gave the quinoxaline derivative (**10**), though only under severe conditions.[14] Reduction with sodium borohydride gave the colourless 4,5-diol (**11**) (of undetermined configuration), which was reconvertible into the starting material (**9**) by Kiliani oxidation.[5] Ring *C* incorporating the α-diketo grouping was cleaved by alkaline hydrogen peroxide as expected:[15] the resulting dicarboxylic acid (**12**) and its dimethyl ester (**13**) retained the IR absorption of their preserved γ-lactone moiety. Significantly, the α-diketone (**9**), lacking an activated methylene group, failed to undergo bromination, a reaction that occurs readily[2] at C-4 of its monoketo precursor (**2**). Conversely, the 4-bromo-5-ketone product (**14**) was unaffected by selenium dioxide, the position adjacent to C-5 being now unavailable for oxidation by this reagent.

The action of Grignard reagents on the keto lactone (**2**) gave good yields of the cyclic tertiary alcohols (**3**) and (**4**). The alicyclic keto absorption[2] changed to a prominent hydroxy peak, while the γ-lactone band persisted. The 5-keto group of compound (**2**) thus reacted normally,[16] but its tetrahydro-



Scheme 1. *Reagents:* i, RMg X; ii, H_2/Pt; iii, $NaBH_4$; iv, $LiAlH_4$; v, CrO_3; vi, SeO_2; vii, H_2O_2, OH^-; viii, CH_2N_2.

furanone component was unaffected by the Grignard reagents, in spite of their presence in a large excess. In contrast, the parent γ-butyrolactone is known to react with methylmagnesium iodide, with simultaneous ring cleavage, to yield 4-methylpentane-1,4-diol.[17] Its failure to react analogously as part of the spirolactone structure (**2**) is further confirmed by the inertness of the secondary alcohol (**7**)[2] towards Grignard reagents; it is ascribed to steric hindrance exerted, in substrate (**2**), by the 4′,4′-dimethyl group adjacent to the 5′-keto function and, to a lesser degree, by the more remote bulky bicyclononane framework, projecting on either side of the plane containing the 5′-keto function.

The action of acetic anhydride–perchloric acid on tertiary alcohol (**3**) resulted in dehydration involving the tertiary hydroxy group rather than its acetylation, producing the cyclic olefin (**5**). Catalytic hydrogenation (H_2/Pt) reduced both its isolated double bond and phenyl moiety to yield the fully saturated product (**6**). The hydrogenation of aromatic components of comparable alicyclic systems is on record.[18] In compounds (**3**) and (**6**) the bulky phenyl or cyclohexyl substituent is likely to assume a quasi-equatorial position with respect to the bicyclononane core, so as to minimise steric interference within the structure. These reactions of the keto lactone (**2**) are summarised in Scheme 1.

^{13}C *NMR Spectra.*—The assignment of the ^{13}C NMR spectra of the compounds now described (Table 1) is ultimately based on comparisons with that of the prototype (**2**), which has been mapped reliably by the INADEQUATE technique[2] and is included for reference in the Table. The chemical shifts of the individual positions in the ring sytem (**C**), (**D**) are virtually constant: coupled with their response to structural changes at specific centres, they provide consistent support for the proposed formulations throughout the series. The salient spectral characteristics of the carbon framework have been discussed before[2] and apply equally to the present examples; further comment is restricted to such additional features as emerge from the new data.

The spectrum of the α-diketone (**9**) is almost coincident with that of its precursor (**2**), except for deviations associated with centres in the immediate environment of the structural change. The new 4-keto group produces an additional low-field singlet, and deshields the adjacent C-3 carbon by its electron-withdrawing effect.

The conversion of the 5-ketone (**2**) into the tertiary alcohols (**3**) and (**4**) [and indirectly lactone (**6**)] produced the appropriate responses in the signal of C-5, as well as a small deshielding of the proximate 3-*gem*-dimethyl carbons. In compound (**6**), the 5-cyclohexyl substituent appears to exert an inductive effect comparable to that of electron-releasing branched alkyl groupings (*e.g.*, $CHMe_2$), shown by the distinct shielding of the adjacent carbon atoms (C-4, -6). For lack of

Table 1. Carbon NMR spectral data and their assignment.[a]

Compound[b]	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9
(2)	41.5 s	54.3 t	32.7 s	54.1 t	211.3 s	62.5 d	91.9 s	50.9 t	39.6 t
(7a)	40.6 s	57.3 t	31.7 s	43.0 t	72.8 d	53.3 d	93.7 s	55.2 t	39.0 t
(9)	41.7 s	*54.1 t	45.2 s	+207.9 s	+210.1 s	62.8 d	90.4 s	*52.3 t	39.0 t
(4)	40.8 s	*54.1 t	32.2 s	55.8 t	75.0 s	60.1 d	96.1 s	53.0 t	40.0 t
(3)	40.6 s	*55.3 t	33.0 s	*56.0 t	77.2 s	58.2 d	97.0 s	50.9 t	40.4 t
(6)	41.9 s	*58.6 t	32.8 s	+44.8 t	°49.6 d	°40.9 d	95.7 s	*55.6 t	+41.4 t
(12)[f]	41.6 s	53.2 t	42.0 s	185.6 s	179.1 s	54.5 d	90.7 s	55.8 t	45.1 t
(13)[f]	41.4 s	53.6 t	42.0 s	178.8 s	173.8 s	54.4 d	90.9 s	55.8 t	45.3 t

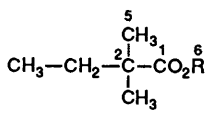
Compound[b]	C-10	C-11 ax	C-12 eq	C-3′	C-4′	C-5′	C-6′	C-7′	C-X
(2)	32.1 q	29.8 q	34.4 q	41.9 t	39.4 s	181.2 s	24.6 q	25.3 q	
(7a)	33.1 q	31.4 q	37.1 q	42.8 t	40.5 s	181.5 s	25.8 q	26.2 q	Ac[c]
(9)	32.3 q	26.5 q	27.1 q	43.2 t	40.6 s	180.7 s	25.5 q	26.2 q	
(4)	33.3 q	33.0 q	34.4 q	44.2 t	40.4 s	182.3 s	*26.0 q	*26.2 q	5-Me[c]
(3)	*34.2 q	*33.3 q	36.5 q	44.8 t	40.7 s	182.1 s	+25.9 q	+26.3 q	Arom[d]
(6)	*33.5 q	*32.0 q	37.7 q	44.2 t	40.7 s	181.6 s	26.0 q	26.6 q	C_6H_{11}[e]
(12)[f]	*27.2 q	*26.8 q	*26.4 q	44.2 t	40.1 s	181.3 s	*26.0 q	*25.9 q	
(13)[f]	*27.4 q	*27.1 q	*26.5 q	44.5 t	40.0 s	181.1 s	26.0 q	25.8 q	51.8 q,[g] 51.7 q

[a] The Table records the proton noise-decoupled chemical shifts and first-order multiplicities of the individual signals. Chemical shifts are given in δ-values downfield from $SiMe_4$. The solvent was deuteriochloroform. [b] The numbering of the ring system is given in structure (C), and that of the exocyclic carbon atoms in structure (D). The signals of the spiro-carbon are recorded as C-7; consequently there is no entry for C-2′. [c] The extranuclear 5-methyl carbon of compound (4) produces an additional quartet at δ_C 37.8. The acetyl carbons of monoacetate (7a) produced additional signals at δ_C 169.5 s and 21.5 q. [d] The aromatic moiety of compound (3) produces the following additional signals: δ_C 148.8 s, 127.4 d, 128.4 d, and 125.5 d, the last two of double intensity. [e] The cyclohexyl substituent in compound (6) produces the following additional signals: δ_C 44.0 d, 33.3 t, 32.3 t, 26.5 t, 26.4 t, and 26.3 t. [f] The carbon atoms of the two ring-*A*-opened compounds (12) and (13) are numbered, in this Table *only*, shown in Scheme 1, so as to maintain a direct comparability of signals in both the tricyclic and ring-cleaved structures. This numbering differs from the systematic nomenclature appearing in the Experimental part. [g] Methyl carbon of the methoxycarbonyl groups. *,+,° Figures may be interchanged horizontally.

strictly comparable precedents, the assignment of the three doublets of compound (6) remains uncertain: the signal at δ_C 44.0 is provisionally allocated to the methine carbon of the cyclohexyl substituent (Table 1, note *e*), being closest to that of the corresponding (but not entirely analogous) centre in bicyclohexyl[19] (δ_{CH} 44.9) and (cyclohex-1′-enyl)cyclohexane[20] (δ_{CH} 46.6).

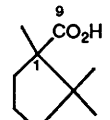
In the ring-C-opened diacids (12) and (13), the chemical shifts of the intact γ-lactone ring-carbons are almost unaffected, but the alterations elsewhere in the molecule are reflected in appropriate spectral changes. The new carboxyl groups (C-4, -5) are differentiated by reference to the assigned spectra of 2,2-dimethylbutanoic acid and its methyl ester[21] (E), (F) and the cyclopentanedicarboxylic acid (G).[22] In the former, the chemical shifts of the carboxyl terminus and its two adjacent carbon atoms [C-1, -2, and -5 in (E) and (F)] agree closely with those allocated to the 1-side-chain of compounds (12) and (13) (*i.e.* C-4, -3, -11, and -12). The remaining carboxyl singlet of compounds (12) and (13), assigned to C-5 by exclusion, matches in its resonance that of the comparable centre in diacid (G) (C-10). The signals of the acid (12) and its methyl ester (13) are almost identical, except for the expected[23,24] displacement of the ester carbonyl singlets to slightly higher field.

The proposed allocation of the quartets to the *gem*-dimethyl groups (C-11, -12 and -6′, -7′) is guided by the general rule[25,26] that the *axial* component of such groups in condensed cyclohexane systems is associated with the signal at *higher* field. In the present case, these guidelines discriminate between the methyl groups in terms of their axial–equatorial conformation, but do not specify their position (α or β) with respect to the plane of the rings. Thus, in the cycloheptane ring *C* of compound (D),



(E) R = H (F) R = Me

	δ_C	δ_C
C-1	185.5	177.3
C-2	42.7	43.0
C-5	24.6	24.9
C-6		51.3



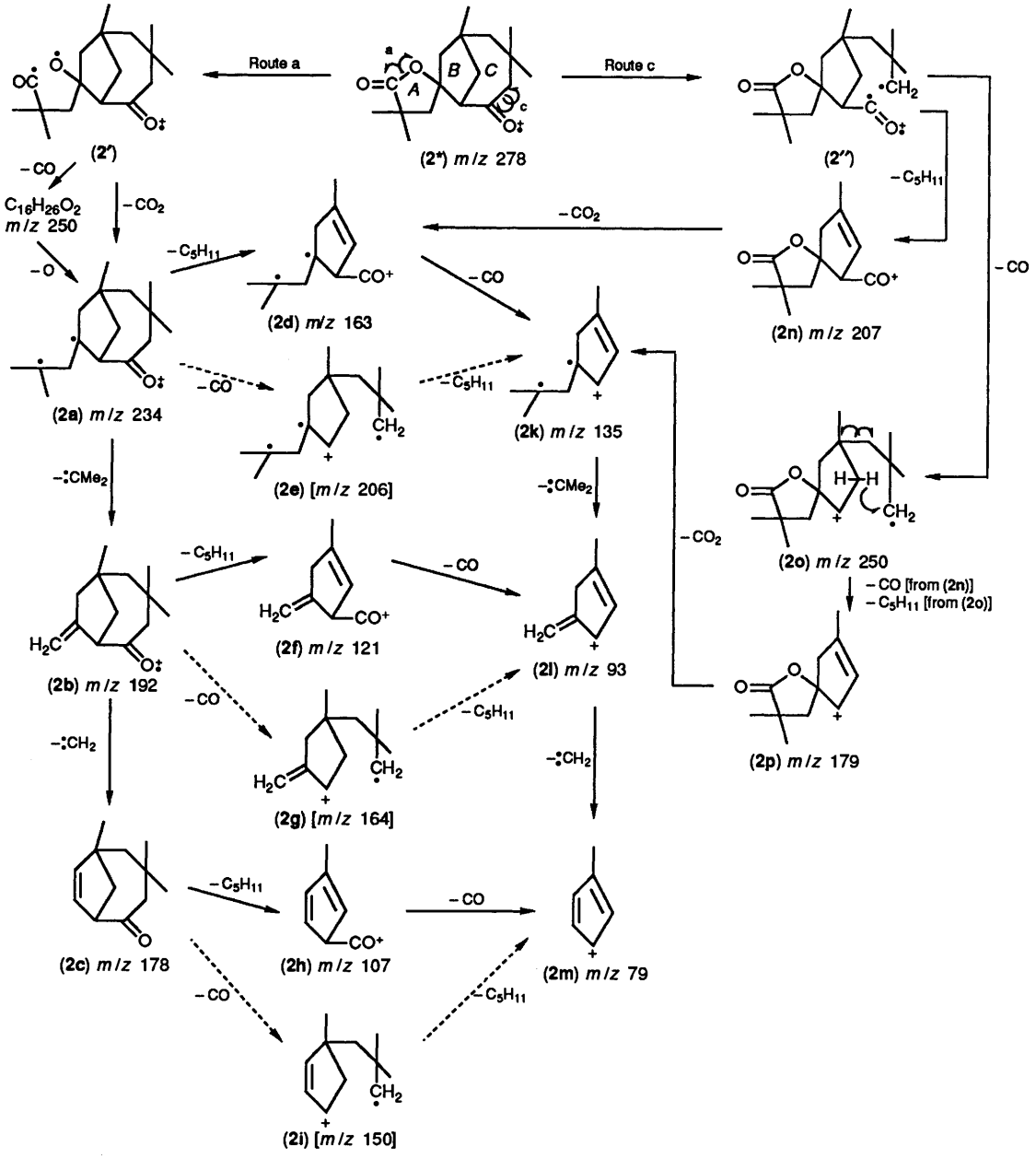
(G)

	δ_C
C-9	175.7
C-10	177.6

itself of uncertain conformation, rotational isomerisation ('flipping') at its C-3 position reverses the relative locations of its *gem*-dimethyl attachments. On balance, the structure favoured on grounds of steric hindrance may be the one in which the 3-CMe_2 grouping assumes the 3β(ax)/α(eq)-configuration.* In the γ-lactone ring of compound (D), conformational differences within the 4′-*gem*-dimethyl-group are less distinct: Its two halves are spaced approximately symmetrically with respect to the near-planar 5-membered ring[27] and consequently differ only little in their chemical shifts. Similarly, partial flattening of ring *C* by the 4,5-diketo grouping in compound (9) modifies the consistently unequal chemical shifts of the adjacent 3-*gem*-dimethyl group to nearly identical values. Again, ring-C-opening (2) ⟶ (12), (13) equalises the chemical shifts of the C-11, -12 quartets; the fact that they are not absolutely coincident suggests that the 1-side-chain is subject to a small configurational constraint by the molecule as a whole.

Mass Spectra and Fragmentation Patterns.—The mass spectra of the bicyclononane-spiro-(tetrahydrofurans) (D) provide further data in support of the structural assignments.

* In this description, the *upper* face of rings *B*/*C* is the one on the side of the 1-*O*-heteroatom of ring *A*.

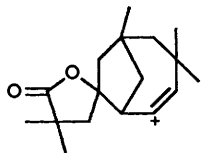


Scheme 2.

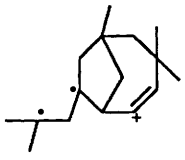
They reveal a consistent fragmentation pattern comprising the removal of rings *A* and *C* by essentially constant pathways. Degradation of ring *A* occurs by successive loss of the elements of carbon dioxide, and of the dimethylmethylene (:CMe_2, possibly as isopropylidene) and methylene radicals (:CH_2), while that of ring *C* involves the loss, in either sequence, of the neopentyl ($^{\bullet}CH_2CMe_3$) or isobutyl ($^{\bullet}CH_2CHMe_2$) radical, and those residual parts of the seven-membered ring *C* that are not common to the cyclopentane core *B*. The simple pentadienyl ions (**2l**), (**2m**); (*m/z* 93, 79) are the terminal cyclic scission products in every case. Although conforming to a common overall pattern, the process may proceed by one or more of several permutations of its component parts. The prevalence and sequence of its branches varies with the substitution pattern of the individual compounds. Scheme 2 illustrates the proposed fragmentation of the prototype (**2**) in some detail, with the object of providing a comprehensive model for interpreting the group of mass spectra as a whole.

The initial fission of the molecular ion (**2***) is thought to occur, as is usual,[28] at the bonds adjacent to the keto group of rings *A* or *C*. The signals of the prototype (**2**) [and its closest analogues (**1**), (**9**), and (**14**)] suggest that ring-*C* fission predominates in the early stages of the degradation. The cleaved molecular ion (**2″**) yields, by loss of carbon monoxide, the intermediate (**2o**), from which the 1-side-chain is removed with simultaneous intramolecular radical transfer of one of the 9-hydrogen atoms to the leaving neopentyl radical ($^{\bullet}CH_2CMe_3$, *m/z* 71). The mechanism of this step (**2o**) ⟶ (**2p**) is thus identical with that of the comparable loss of ring *C* from the diisophorone structure [*e.g.*, (**B**)].[29] The alternative (possibly more plausible) disposal of the leaving 1-side-chain as *gem*-dimethylcyclopropane (*m/z* 70), observed in the case of diisophorones,[29,30] is not found in the present series, peaks indicative of this process being absent. The degradation is completed by the stepwise dismantling of ring *A* (**2p**) ⟶ (**2k**) ⟶ (**2l**) ⟶ (**2m**): the ready generation of ions by loss of carbon dioxide from γ-lactones and their methylated homologues is well documented.[31] The conversely less con-

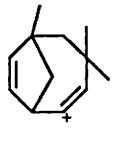
spicuous sequence, starting with fission of ring *A*, is indicated by the appearance of the signal peak of *m/z* 192 of medium intensity, assignable to the radical ion (**2b**). A group of additional prominent signals (*m/z* 207, 163, 121, 107) are compatible with the preferential loss [from (**2″**)] of the neopentyl radical, and retention of the 5-carbonyl moiety during the degradation of ring *A* (**2″**) ⟶ (**2n**) ⟶ (**2d**) ⟶ (**2f**) ⟶ (**2h**); members of this pathway possibly also arise by 'transverse' routes of the general scheme: all the alternatives lead to the molecular ion (**2m**) as the common cyclic end-product. Branches proceeding by way of the potential intermediates (**2e**), (**2g**), and (**2i**) (broken arrows) do not apparently contribute to the fragmentation of the prototype (**2**) but, occurring in other examples [*e.g.*, (**2i**) from (**2**) oxime], are included for the sake of completeness.



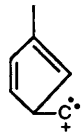
(**2q**)



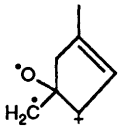
(**2r**) *m/z* 217



(**2s**) *m/z* 161



(**2t**) *m/z* 91



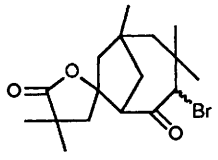
(**2u**) *m/z* 109

A fragmentation sequence additional to Scheme 2 appears to commence with the loss of the 5-hydroxyl radical from the enolised ketone [giving (**2q**)]. The signals of varying intensity at *m/z* 217 and 161 [in the spectra of compounds (**1**), (**2**), (**14**), (**15**), (**16**)] are attributable to the derived species (**2r**) and (**2s**); further scission of the latter *via* (**2t**) [to afford (**2m**)] is suggested by the frequent appearance of the signal having *m/z* 91.

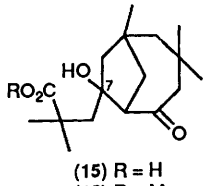
In the oxime of compound (**2**), the 5-hydroxy imino substituent reverses the relative stability of rings *A* and *C*: decomposition occurs chiefly by the breakdown of ring *A*, either directly (*m/z* 293 ⟶ 249 ⟶ 207 ⟶ 193) or after loss of the 5-hydroxy group (*m/z* 276 ⟶ (260, 248) ⟶ 232 ⟶ 176), followed by the usual supplementary scissions [to (**2m**)]. Its base peak (*m/z* 109) (a constant though less prominent feature of nearly all the other spectra) is not accommodated by Scheme 2; it is thought to correspond to structure (**2u**) (possibly as the cyclised spiro-oxirane), arising by the alternative scission of the γ-lactone ring *A* at its 1,5-bond.

The carboxylic acid (**1**) produces a mass spectrum substantially identical with that of the keto lactone (**2**), showing that, after preliminary decarboxylation, it undergoes the standard fragmentation, as does the α-bromo ketone (**14**) after ejection of its halogen substituent.

Fragmentation patterns based on Scheme 2 similarly interpret the behaviour under electron impact of other members of the tricyclic ring system (**D**). They are not shown individually but may be produced readily in accordance with the following brief outlines.



(**14**)

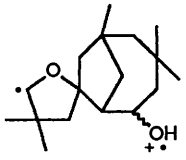


(**15**) R = H
(**16**) R = Me

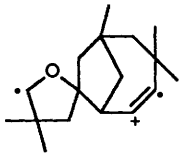
The diketone (**9**) undergoes fragmentation at its ring *C* with sequential loss of the two keto groups and the remaining 1-substituent, the latter as the usual[29] isobutyl radical (*m/z* 264, 236, 179). Subsequent stepwise removal of ring *A* (*m/z* 163, 135, 93, 79) terminates in the common species (**2m**). The inverse sequence of events may be the source of some of the intermediate peaks (*e.g.*, *m/z* 149, 107).

The fission of the ring-*A*-opened bicyclic hydroxy carboxylic acid[2] (**15**) and its methyl ester (**16**) conforms essentially to Scheme 2, but is more diverse as indicated by the greater complexity of their spectra. A series of prominent signals indicates the successive degradation of rings *C* and (cleaved) *A* [*m/z* 296, 225, (197), 152, 135, 93, 79]. Simultaneous dehydrative recyclisation (to ring *A*) gives rise to the parallel line of peaks corresponding to the sequence (**15**) ⟶ (**2″**) ⟶ (**2n**) ⟶ (**2p**), while an alternative branch proceeds with retention of the 5-carbonyl group [*m/z* 225, (180), 163, 121, 107, 79]. Additional strong signals suggest that the 7-substituents may function as the first targets of the electron attack (*m/z* 209, 195, 167).

The 5,5′-dihydroxy compound (**8**), the only example in our study incorporating a reduced γ-lactone ring, appears to eliminate both hydroxy groups preferentially. The resulting species (**8a**) and (**8b**) yield fragments by degradation of rings *A* and *C* [especially from (**8b**)] according to the general scheme. The 4,5-dihydroxy compound (**11**) is cleaved, after preliminary dehydration at its glycol moiety, by the sequential loss of the isobutyl radical and the components of the residual 6-substituent from ring *C* (*m/z* 296, 278, 221, 209, 191, 179). From each of these intermediates, ring *A* is in turn removed in the usual stages to produce fragments accounting for nearly all the numerous signals. Additional peaks of medium intensity suggest that demethylation, presumably from C-1, makes a minor contribution (*m/z* 263, 237, 180, 163).



(**8a**) *m/z* 265



(**8b**) *m/z* 247

Demethylation is a more prominent feature of the fission of the 5-hydroxy compound (**7**) and its acetyl derivative (**7a**). A sequence of signals indicates, after preliminary dehydration, the stepwise degradation of ring *A* (*m/z* 280, 262, 218, 176, 162); a parallel set of peaks corresponds to the same changes with simultaneous loss of a fragment having *m/z* 15 (*m/z* 262, 247, 203, 161, 147). Degradation of ring *C* of the intermediates by elimination of ·CH_2CHMe_2 and ·CH=CH· moieties (*m/z*) 57 and 26) from the former sequence, and of ·CH_2CMe_2· and ·CH=CH· moieties (*m/z* 56 and 26) from the latter, accounts for several of the remaining signals (*m/z* 205, 161, 135; and 191, 147, 121, respectively). The terminal cyclic fragments are again the usual pentadienes (*m/z* 93, 79).

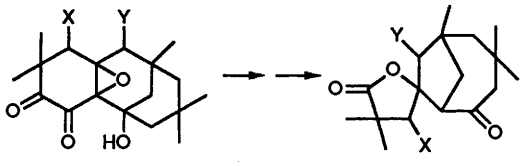
The fission of the tertiary alcohols (**3**) and (**4**) involves the initial elimination of their 3-alkyl (or aryl) substituent and the elements of water from ring *C*. The Δ^4-unsaturated centre thus introduced again stabilises ring *C* relative to *A*; stepwise removal of the latter finally produces (**2s**) as the most abundant molecular ion (base peak, *m/z* 161). Loss of the ·CH_2CMe_2· radical therefrom accounts for the second prominent signal (*m/z* 105) emitted by both compounds (**3**) and (**4**). The other numerous signals are identifiable according to Scheme 2: they correspond to individual fragments of several simultaneous pathways, none of them traceable in full. It must be concluded

Table 2. Mass spectra data of bicyclo[4.2.1]nonane-7-spiro-2′-(tetrahydrofurans).

Compd.	(1)	(2)	(2a)[a]	(14)	(9)	(15)	(16)	(7)	(7a)	(8)	(11)	(3)	(4)
mol wt	322	278	293	357	292	296	310	280	322	282	296	356	294
				358 w									
				356 w									
	322 w	278 w	293 m	343 w	292 m	296 w	310 w	280 w	322 w		296 w	356 w	294 w
				341 w			295 w		307 w			338 w	
	304 w			330 w								323 w	
	286 w			328 w									
	278 m		278 m	277 vs		278 m	278 w		280 w		278 w		279 w
	276 m		276 s					265 w		265 vs			276 w
	260 w	260 s	260 w	259 m	264 w	263 m	263 m	262 w	262 s		263 w	261 w	261 m
	250 w	250 m	249 w	249 m			249 w			249 m	252 w	252 w	
			248 w			245 w	245 w	247 m	247 s	247 vs			
	232 w	232 m	232 w	233 vs	236 w	235 w	239 s	234 w	234 m	236 m	234 w		232 w
		219 m		219 s	221 m	225 s	222 w			231 m	221 m	223 s	223 w
	217 m	217 m		217 s		217 w	217 w	218 m	218 s	218 m			217 w
						209 s	209 s			217 m	209 m		207 m
	207 s	207 w	207 s		207 w	207 m	207 s	203 w	205 vs				205 m
	192 m	192 m	193 s		193 w	195 s	195 s	191 w	191 w	194 m	191 m		
		181 m				191 m		181 m		180 m	180 m	181 m	
	179 vs	179 m			179 w	179 m	179 s	179 m	179 m	178 m			177 w
			176 w		177 w			176 vs	175 m	176 s			
	163 s	163 vs		163 s	163 vs	163 w		162 m	162 m	162 m	165 m		
	161 vs		161 w	161 m		161 w	161 w	161 m	161 s	161 m	163 m	161 vs	161 vs
		153 s	152 s			153 s	152 vs				161 m	150 s	150 vs
	147 m	152 vs	150 vs	151 s	149 m	152 vs		147 s	147 s	147 m	147 s		
	139 m	139 vs		139 s	139 vs	139 vs	139 vs	137 vs	137 vs		137 s		
	135 vs	135 vs	135 s	135 vs	135 vs	135 s	135 m	136 vs		135 vs	135 vs	135 m	135 s
	123 m		134 s			123 s	123 s	135 vs		123 vs	123 s		
	121 m	121 m	124 s	121 vs	121 vs	121 m	121 s	121 s	121 vs	121 s	121 s	121 m	121 s
		109 s	109 vs	109 vs	109 m	109 m	115 vs				109 vs		118 m
	107 s	107 s		107 s	107 s	107 m	107 m	107 vs	107 vs	107 s	107 s	105 vs	105 s
		97 vs		97 s		97 vs	97 vs					95 s	95 s
	93 s	93 s	93 vs		93 vs	93 s		93 vs	93 vs	93 vs	93 vs	93 m	93 m
	91 s	91 m	91 s	91 s		91 m	91 m	91 m	91 m	91 m	91 s	91 s	
		83 vs		83 vs	81 vs			81 vs	81 vs	81 s	81 s		
	77 s	79 s	79 vs			79 m	73 vs	79 s		79 m	79 s	79 m	79 m
	69 s	69 s	67 m	69 s	69 s	69 vs	69 vs	69 vs	69 vs	69 vs	69 s	69 m	69 m
	55 vs	55 vs	55 s	55 vs	55 vs	55 vs	55 vs	55 vs	55 vs	55 vs	55 vs	55 s	55 vs
	41 vs	41 vs	41 vs	41 vs	41 vs	41 vs	41 vs	41 vs	43 vs	41 vs	41 vs	41 s	41 vs

[a] Compound (**2a**) is the oxime of (**2**).

that the tertiary alcohols are cleaved less uniformly than the other members of the series. Mass spectral data are presented in Table 2.



Conclusions.—In spite of the restricted access to the present ring system by the oxidative rearrangement of the epoxy diketone (**B**), so far represented by a single example (**B**) ⟶ (**1**), several of its members are made available for study by interconversions within the structural pattern. The direct synthetic route might be broadened, and its proposed reaction mechanism[2] further tested by extending it to 6- and/or 8-substituted analogues of (**B**), the production of which would be a profitable task. It is recalled that no structural alteration affecting ring *C* of the tricyclo[7.3.1.$0^{2,7}$]tridecane ring system (**A**) or (**B**) has so far been observed in its numerous substitution reactions.

Experimental

General.—Details concerning reagents, solvents, and general procedures, as well as the equipment used in obtaining the spectral data, are as specified in Part 23 of this series.[2] Unassigned IR peaks are not listed except for the prototypes (**8**), (**9**), and (**3**). M.p.s are uncorrected.

5-Hydroxy-1,3,3,4′,4′-pentamethylbicyclo[4.2.1]*nonane-7-spiro-2′-(tetrahydrofuran)-5′-one* (**7**).—A solution of the keto lactone (**2**)[2] (2.78 g, 10 mmol) in warm ethanol (75 ml) was cooled to room temperature and treated with sodium borohydride (1.05 g, 30 mmol) in portions (effervescence). The suspension was set aside for 2 h, and the nearly clear liquid was poured into stirred ice–water (300 ml) containing hydrochloric acid (40 mmol). The initially soft precipitate gave, on crystallisation from ethanol–light petroleum (6 and 60 ml), microprisms (2.25 g, 80%) of title compound (**7**), identified by mixed m.p. 158–160 °C and IR spectroscopy, and by its conversion into the 5-*O*-acetyl derivative (**7a**), m.p. 135–137 °C. The procedure is superior to the catalytic hydrogenation previously described.[2]

1,3,3,4′,4′-Pentamethylbicyclo[4.2.1]*nonane-7-spiro-2′-(tetrahydrofuran)-5,5′-diol* (**8**).—(*a*) A solution of the keto lactone (**2**)[2] (1.39 g, 5 mmol) in diethyl ether (120 ml) was added to a stirred

suspension of lithium aluminium hydride (0.57 g, 15 mmol) in (sodium-dried) diethyl ether (50 ml), and the reaction mixture was boiled under reflux for 2 h. The excess of the reducing agent was destroyed by addition of 1.5M-hydrochloric acid, and the product was extracted with diethyl ether. The residual glass-like solid (1.0–1.2 g, 70–84%) obtained from the washed and dried (Na_2SO_4) extracts gave, on crystallisation from benzene, platelets of the *5,5'-diol* (**8**), m.p. 158–160 °C (Found, for a sample kept at 110 °C/2 mmHg for 2 h: C, 71.9; H, 10.7%; *M* (mass spectrometrically) 282. $C_{17}H_{30}O_3$ requires C, 72.3; H, 10.6%; *M*, 282); ν_{max} 3 340–3 235vs br (OH), 2 950–2 900 vs, 1 480, 1 475s d, 1 460s sh (Me, CH_2), 1 390m, 1 365ms (CMe_2), 1 045s, 1 030s (C–O of C–OH), 1 335m, 1 005s, 1 000s, and 965m cm^{-1}.

(*b*) The use of the 5-hydroxy spirolactone (**7**) (1.40 g, 5 mmol) in the foregoing procedure gave the same 5,5'-diol (**8**) (64–75%), identical (mixed m.p., IR) with material obtained in (*a*).

(*c*) *Reoxidation to the starting material.* A solution of the diol (**8**) (0.28 g, 1 mmol) in acetone (8 ml) was treated with Kiliani's 10% chromic acid [5] (1.75 ml, 1.5 mmol) and set aside at room temperature for 4 h. It then was poured into stirred water (120 ml); the precipitate which gradually separated (65%) was identified, after crystallisation from light petroleum, as compound (**2**) by mixed m.p. (94–97 °C) and IR spectroscopy.[2]

1,3,3,4',4'-Pentamethylbicyclo[4.2.1]*nonane-7-spiro-2'-(tetrahydrofuran)-4,5,5'-trione* (**9**).—A solution of the keto lactone (**2**)[2] (0.56 g, 2 mmol) in glacial acetic acid (12 ml), treated with selenium dioxide (0.28 g, 2.5 mmol), was boiled under reflux for 5 h, the black selenium was filtered off, and the deep-yellow filtrate was stirred into water (100 ml). The air-dried precipitate gave, on crystallisation from ethanol–water (3:1) or preferably from light petroleum, pale yellow prisms (0.26–0.33 g, 45–66%) of the *α-diketo lactone* (**9**), m.p. 112–114 °C (Found: C, 69.9; H, 8.4%; *M*, 292.$C_{17}H_{24}O_4$ requires C, 69.9; H, 8.2%; *M*, 292). No significant absorption in the near-UV range; ν_{max} 2 985s, 2 885ms, 1 475m, 1 460–1 450m br (Me, CH_2), 1 770vs (CO, γ-lactone), 1 700vs (CO, α-diketone), 1 395m, 1 370ms (CMe_2), 1 240s (C–O–C), 1 335m, 1 320m, 1 295m, 1 210m, 1 145m, 1 100m, 965m, 930m, 910m, and 740m cm^{-1}.

4-Bromo-1,3,3,4',4'-pentamethylbicyclo[4.2.1]nonane-7-spiro-2'-(tetrahydrofuran)-5,5'-dione (**14**) failed to react under the foregoing conditions, being recovered (60%) after its solution in glacial acetic acid (1 mmol in 15 ml) was boiled with selenium dioxide (3 mmol) for 5 h.

Quinoxaline Derivative (**10**).—A mixture of the α-diketo lactone (**9**) (0.29 g, 1 mmol) and *o*-phenylenediamine (1.08 g, 10 mmol) was heated to boiling point, then kept at 200–210 °C for 5 min. The solidified dark-brown melt was heated with glacial acetic acid (4 ml) at 100 °C for 5 min, and poured into stirred 0.5M-hydrochloric acid (60 ml). Crystallisation of the pink precipitate from ethanol (5 ml) gave ivory platelets (52%) of the *quinoxaline* (**10**), m.p. 169–171 °C (Found: C, 75.7; H, 8.5; N, 8.0. $C_{23}H_{28}N_2O_2$ requires C, 75.8; H, 7.7; N, 7.7%); ν_{max} 2 980vs–2 870s, 1 480ms d, 1 460s (Me, CH_2), 1 760vs br (CO, γ-lactone, ? C=N), 1 390m, 1 360m (CMe_2), 775vs, and 765vs (*o*-disub. benzene) cm^{-1}. Interaction did not occur in boiling ethanol or dimethylformamide (6 h), the reactant being substantially recovered.

4,5-Dihydroxy-1,3,3,4',4'-pentamethylbicyclo[4.2.1]*nonane-7-spiro-2'-(tetrahydrofuran)-5'-one* (**11**).—A solution of the diketo lactone (**9**) (0.29 g, 1 mmol) in ethanol (20 ml) was treated with sodium borohydride (0.19 g, 6 mmol) and the gently effervescing suspension was set aside at room temperature for 2 h; it cleared within *ca.* 40 min. Addition to water precipitated a white solid (48%), which gave platelets of the *4,5-diol* (**11**), m.p. 177–179 °C (from ethanol–light petroleum) (Found: C, 68.9; H, 9.2%; *M*, 296. $C_{17}H_{28}O_4$ requires C, 68.9; H, 9.5%; *M*, 296); ν_{max} 3 570–3 535s d (OH), 2 940–2 915s br, 2 870s, 1 455ms br (Me, CH_2), 1 390ms, 1 370m (CMe_2), 1 720vs (? CO, γ-lactone), and 1 240ms (C–O–C) cm^{-1}.

The diol (**11**) was reconverted by Kiliani's 10% chromic acid [5] into the starting material (**9**), identified by mixed m.p. and IR spectroscopy.

Resistance of Compound (**9**) *to Bromination.*—The diketo lactone (**9**) was substantially recovered (60%) after treatment with bromine in glacial acetic acid in the presence of 60% hydrobromic acid under the usual conditions [2] (no decolourisation).

Ring-C Cleavage of Compound (**9**) *to 4'-(2-Carboxy-2-methylpropyl)-4,4,4'-trimethyl-5-oxotetrahydrofuran-2-spiro-cyclopentane-2'-carboxylic Acid* (**12**).—A solution of compound (**9**) (0.29 g, 1 mmol) in warm methanol (10 ml) was treated with 30% hydrogen peroxide (2.3 ml, 20 mmol), followed by 3M-sodium hydroxide (1 ml, 3 mmol), when the yellow colour was discharged at once. After storage for 30 min most of the solvent was removed under reduced pressure, the residual liquid was added to ice, and the mixture was acidified with 3M-hydrochloric acid. The precipitated oil solidified (yield 60–70%) and gave, on crystallisation from ethanol–water (3:1), opaque granules of the *dicarboxylic acid* (**12**), m.p. 138–141 °C (Found, for a sample kept at 110 °C/3 mmHg for 4 h: C, 62.9; H, 8.6. $C_{17}H_{26}O_6$ requires C, 62.6; H, 8.0%); ν_{max} 2 970vs–2 880s, 1 475–1 440ms tr (Me, CH_2), 2 670–2 550ms (OH of CO_2H), 1 780vs (CO, γ-lactone), 1 705vs, 1 690vs (CO of CO_2H), 1 395m, 1 370ms (CMe_2), 1 240s (C–O), 1 200vs, 1 175vs, 1 130s, and 930vs cm^{-1}.

Dimethyl Diester (**13**).—A stirred solution of the foregoing dicarboxylic acid (**12**) (0.33 g, 1 mmol) in diethyl ether (15 ml) was treated with ethereal diazomethane [prepared [32] from *p*-tolylsulphonyl(methyl)nitrosamine 'Diazald' (1.7 g, 8 mmol)]. The yellow liquid was set aside at room temperature for 2 h, and the excess of the reagent destroyed with 2M-acetic acid. The crude product, isolated in the usual manner, gave, on crystallisation from light petroleum, the *dimethyl ester* (**13**) as needles (56%), m.p. 61–63 °C (Found: C, 64.3; H, 8.5. $C_{19}H_{30}O_6$ requires C, 64.4; H, 8.5%); ν_{max} 2 970–2 850vs, 1 480ms, 1 465ms, 1 455, 1 445s d (Me, CH_2), 1 390m, 1 360s d (CMe_2, Me of ester), 1 760vs (CO, γ-lactone), 1 720vs (CO or CO_2Me), 1 235vs (C–O ester), 1 205vs, 1 145vs, and 1 130vs, cm^{-1}.

5-Hydroxy-1,3,3,4',4'-pentamethyl-5-phenylbicyclo[4.2.1]*nonane-7-spiro-2'-(tetrahydrofuran)-5'-one* (**3**).—To a stirred solution of phenylmagnesium bromide [prepared from bromobenzene (3.9 g, 25 mmol), and magnesium (0.48 g, 20 mequiv.) in diethyl ether (100 ml)] was added a solution of the keto lactone (**2**) (0.56 g, 2 mmol) in diethyl ether (25 ml). The reaction mixture was set aside for 2 h, the excess of the Grignard reagent was destroyed by the slow addition of 3M-hydrochloric acid, and the product was isolated from the washed and dried (Na_2SO_4) ethereal solution. Crystallisation of the white solid (0.4–0.45 g, 56–64%) from ethanol (20 ml per g, recovery 75%) gave *compound* (**3**) as silky needles, m.p. 178–180 °C (Found: C, 78.2; H, 9.2%; *M*, 356. $C_{23}H_{32}O_3$ requires C, 77.5; H, 9.0%; *M*, 356); ν_{max} 3 480vs, 3 380s (OH), 2 960–2 880vs, 1 470s, 1 460s (Me, CH_2), 1 740vs (CO, γ-lactone), 1 500m (C=C, Ar), 1 395m, 1 370mw (CMe_2), 1 225s (C–O–C), 700s (Ph), and 1 340m, 1 300m, 1 100m, 1 040ms, 930s and 775ms cm^{-1}.

1,3,3,4',4'-Pentamethyl-5-phenylbicyclo[4.2.1]*non-4-ene-7-spiro-2'-(tetrahydrofuran)-5'-one* (**5**).—A solution of compound

(3) (0.71 g, 2 mmol) in glacial acetic acid (12 ml)–acetic anhydride (1 ml)–60% perchloric acid (8 drops) was set aside at room temperature for 8 h, then added to ice–water. The resulting precipitate [m.p. 116–118 °C (0.40–0.49 g, 60–72%)] gave prismatic needles of the *ene lactone* (**5**), m.p. 121–123 °C (from light petroleum) (Found: C, 81.4; H, 8.9%; *M*, 338. $C_{23}H_{30}O_2$ requires C, 81.7; H, 8.9%, *M*, 338), ν_{max} 2 970vs–2 870s, 1 460–1 445ms (Me, CH_2), 1 760vs (CO of γ-lactone), 1 500w (C=C, Ar), 1 390m, 1 360m (CMe_2), 1 230s (C–O–C), and 700s (Ph) cm^{-1}.

The material was recovered (85%) after being boiled in ethanol (1 mmol in 12 ml)–3M-sodium hydroxide (3 ml) for 5 h.

5-Cyclohexyl-1,3,3,4′,4′-pentamethylbicyclo[4.2.1]*nonane-7-spiro-2′-(tetrahydrofuran)-5′-one* (**6**).—A solution of compound (**5**) (0.34 g, 1 mmol) in glacial acetic acid (12 ml) was hydrogenated at room temperature over Adams' catalyst [from platinum oxide monohydrate[33] (0.1 g, 0.4 mequiv.)]. Hydrogen uptake was complete within 1 h [observed 90 ml; theoretical 19 + 80 ml at NTP]. Dilution of the filtered liquid with water precipitated a solid (90%), which gave *title compound* (**6**) as felted needles, m.p. 159–161 °C (from light petroleum) (Found: C, 80.1; H, 11.1. $C_{23}H_{38}O_2$ requires C, 79.8; H, 11.0%); no absorption in the near-UV range; ν_{max} 2 945vs–2 870s, 1 465m–1 455s t (Me, CH_2), 1 760vs (γ-lactone), 1 390ms, 1 365m d (CMe_2), 1 225s (C–O–C), and 930s cm^{-1}.

5-Hydroxy-1,3,3,4′,4′,5-hexamethylbicyclo[4.2.1]*nonane-7-spiro-2′-(tetrahydrofuran)-5′-one* (**4**).—To a stirred solution of methylmagnesium iodide, prepared from iodomethane (7.0 g, 50 mmol) and magnesium (0.36 g, 15 mequiv.) in diethyl ether (40 ml) was added a solution of compound (**2**) (0.42 g, 1.5 mmol) in diethyl ether (30 ml) (transient white precipitate). The reaction mixture was set aside for 2 h, the excess of the Grignard reagent was then destroyed, and the crude product was isolated by the standard procedure. The resulting light-brown oil solidified after short storage (0.25–0.32 g, 56–72%) and gave, on crystallisation from light petroleum, lustrous prisms of *title compound* (**4**), m.p. 102–105 °C (Found: C, 72.9; H, 10.3. $C_{18}H_{30}O_3$ requires C, 73.5; H, 10.2%); no significant absorption in near-UV range; ν_{max} 3 495s (OH), 2 965vs–2 880s, 1 485ms, 1 470ms, 1 460ms (Me, CH_2), 1 740vs (CO, γ-lactone), 1 390ms, 1 380ms (CMe_2), 1 240s (C–O–C), 925vs, and 710s cm^{-1}.

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