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PREPARATION AND STRUCTURE OF SOME TRICYCLO[3.2.1.$0^{2,4}$]OCTANE DERIVATIVES

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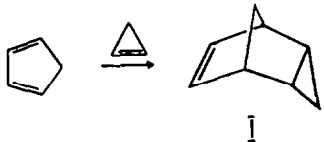
Abstract—The Diels–Alder reaction of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopenta-1,3-diene with cyclopropene has been utilized to furnish some *endo*-tricyclo[3.2.1.$0^{2,4}$]octane derivatives. Several *exo*-tricyclo[3.2.1.$0^{2,4}$]octane derivatives were synthesized from known precursors using standard reactions. The stereochemistry of the tetracyclic alcohol, resulting (ultimately) from the reaction of 7-norbornadienyl acetate with diazomethane, is discussed. The PMR spectra of a number of tricyclo[3.2.1.$0^{2,4}$]octane derivatives are presented and discussed with reference to configurational assignment.

TRICYCLOOCTANE derivatives which contain a cyclopropane ring have been subject to considerable attention of late. In particular, investigations of the solvolysis reactions of such derivatives have been instrumental in defining the stereochemical requirements of cyclopropane participation. The inherent structural rigidity of these tricyclic derivatives makes them ideal substrates for such studies. The recent example of the enhanced, titrimetric solvolysis rate of the *endo*, *anti* isomer relative to the other three isomeric 8-tricyclo[3.2.1.$0^{2,4}$]octyl esters, exemplifies the use of such substrates.[1–3] Related studies on the 6-tricyclo[3.2.1.$0^{2,4}$]octyl system[4,5] and the 3- and 4-tricyclo[3.2.1.$0^{2,7}$]octyl system[6] have been reported.

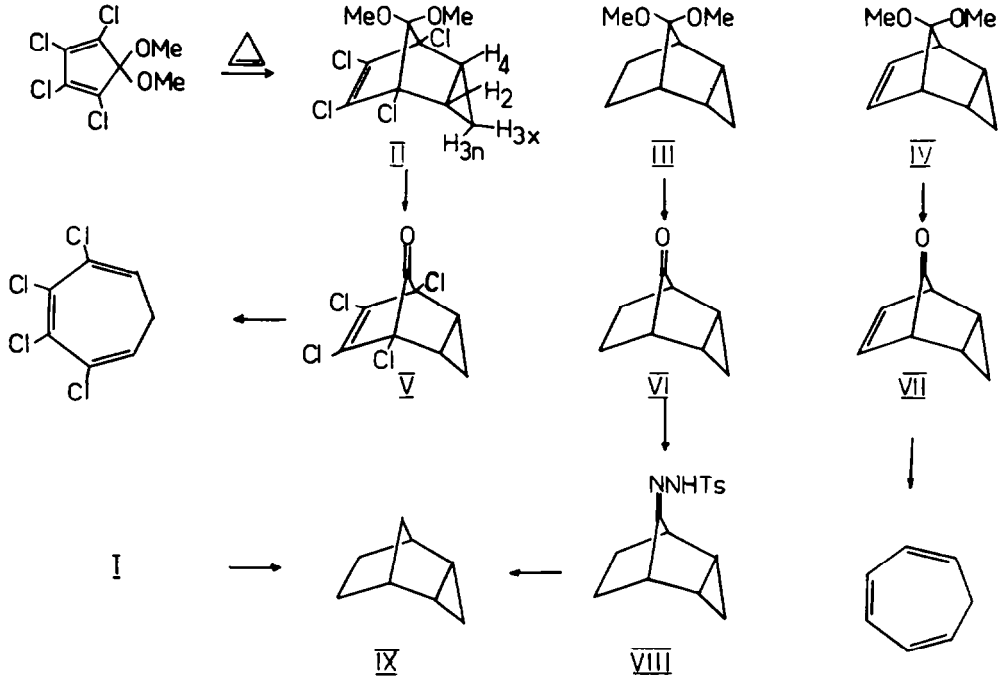
Recent attention has also been concentrated on light induced valence isomerizations of tricyclo[3.2.1.$0^{2,4}$]octenes and compounds with the same basic chromophore.[7–12] Thermally induced isomerizations in the same system have also been reported.[13]



I

In general, synthesis of tricyclo[3.2.1.$0^{2,4}$]octane derivatives formally involves addition of a carbene to a bicyclic olefin. Although reactions of this type may be stereospecific, for the most part isomeric mixtures result. As an alternative route, the Diels–Alder reaction between cyclopropene and cyclopentadiene to give *endo*-tricyclo[3.1.0.$0^{2,4}$]oct-6-ene (I)[14] is attractively simple, particularly in view of the recently reported, convenient preparation of cyclopropene.[15] However, generalization of this reaction to include the preparation of 8-tricyclo[3.2.1.$0^{2,4}$]octane derivatives has never been reported. To our knowledge only one other example of this synthetic approach has appeared in the literature—the preparation of 1,2,3,4,5,6,7-heptaphenyltricyclo[3.2.1.$0^{2,4}$]octan-8-one[16] (presumably *endo*, *exo*). The results of our investigations into the synthesis of 8-tricyclo[3.2.1.$0^{2,4}$]octyl derivatives via this

method are discussed below. Part of this work has been reported in preliminary form.[17] Simultaneously with our preliminary report there appeared two other communications[1,2] dealing with similar synthetic approaches.



RESULTS AND DISCUSSION

The Diels–Alder reaction of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopenta-1,3-diene with cyclopropene gave the tricyclic ketal (II) whose PMR spectrum (see later) was consistent with the assigned structure. Acid catalysed hydrolysis of II yielded the corresponding tetrachloroketone (V) which showed IR absorption at 1855, 1835 and 1800 cm^{-1} characteristic of bridge carbonyl compounds[18] as well as bands at 3060 cm^{-1} (cyclopropane C—H stretch)[19] and 1045 cm^{-1} (cyclopropane ring deformation). The PMR spectrum of V consisted of a typical AMX_2 pattern with $\tau_{H_2} = \tau_{H_4} = 8{\cdot}11$, $\tau_{H_{3x}} = 8{\cdot}35$, $\tau_{H_{3n}} = 9{\cdot}70$ ppm, $J_{H_{3n}H_{3x}} = 8{\cdot}23$, $J_{H_{3n}H_2(H_4)} = 3{\cdot}60$ and $J_{H_{3x}H_2(H_4)} = 7{\cdot}40$ Hz.* The ketone (V) decarbonylated† at the melting point to give 2,3,4,5-tetrachlorotropilidine whose PMR showed two equally intense triplets ($J = 7{\cdot}8$ Hz) at τ 3·90 and 7·50.[2]

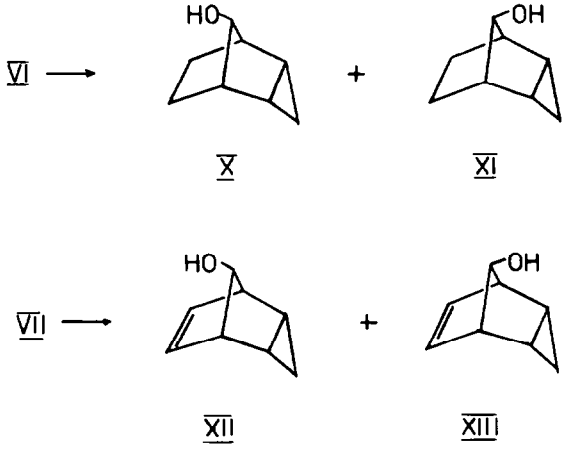
Dechlorination of the tetrachloro ketal (II) according to the method of Winstein[21] resulted in reduction of the double bond and yielded the saturated ketal (III). Mild

* These parameters were obtained by matching of the experimental spectra to computed spectra; unpublished results of R. I. Kagi.

† A systematic study of the decarbonylation of this and related ketones has recently been published.[20] The result of our investigations along these lines will be published at a later date.

acid hydrolysis of III gave the saturated ketone (VI). Although PMR spectroscopy strongly suggested that the cyclopropane ring in II, and consequently in III and VI, was *endo* it was felt that further proof of this was needed. To this end, the saturated ketone (VI) was converted to the tosylhydrazone (VIII) which on subsequent reduction[22] gave *endo*-tricyclo[3.2.1.0^{2,4}]octane (IX). This tricyclic hydrocarbon was identical to the product obtained via catalytic hydrogenation of the known tricyclic olefin (I).[14,15]

The unsaturated ketal (IV) was obtained by dechlorination of II with sodium in *t*-butanol–THF.[23] The PMR spectrum of IV showed the vinyl triplet at τ 4·38, i.e. 0·36 ppm upfield from the vinyl triplet of 7,7-dimethoxynorbornene.[23] This shielding of the vinyl protons in an *endo*-tricyclo[3.2.1.0^{2,4}]octene relative to the vinyl protons in the corresponding bicyclo[2.2.1]heptene is characteristic of the *endo* fused cyclopropane ring in the tricyclo[3.2.1.0^{2,4}]octenes; the vinyl protons of the *exo* fused isomer are deshielded by a similar amount.[3,14,24] Careful hydrolysis of the unsaturated ketal (IV) gave the corresponding ketone (VII) whose PMR spectrum showed the vinyl triplet at τ 3·93 (the vinyl triplet of norbornenone occurs at τ 3·50).[18a] After melting at 30·5–31° the ketone (VII) showed visible signs of gas evolution at about 35° and was quantitatively converted to tropilidene.*



Sodium borohydride reduction of the saturated ketone (VI) gave a 1:1 mixture of alcohols (X and XI). Separation by VPC gave the *endo, anti* alcohol (X) and the known *endo, syn* alcohol (XI).[3] Whereas the *endo, anti* alcohol (X) displayed only one monomeric OH band (3630 cm^{-1}) in the IR the *endo, syn* alcohol (XI) displayed two sharp absorptions (3630 and 3595 cm^{-1}) which we have attributed to free OH and intramolecular bonded OH respectively. The ability of cyclopropane rings to function as proton acceptor groups in H-bonding has recently been discussed in detail by Schleyer[25] and in particular the above two alcohols were included. Mention was also made of the unsaturated epimeric alcohols XII and XIII although at the time only the bonded OH stretching frequencies of the epimers were published.[1]

* A systematic study of the decarbonylation of this and related ketones has recently been published.[20] The results of our investigations along these lines will be published at a later date.

In our hands these epimers showed two OH frequencies: XII at 3625 and 3575 cm^{-1} and XIII at 3630 and 3590 cm^{-1}. The lower position of the bonded frequency in XII relative to that in XIII was used in the first instance to establish configurations of these epimers.[1] Further evidence supporting this configurational assignment is presented below.

These two unsaturated alcohols were obtained (XII 25%, XIII 75%) via sodium borohydride reduction of the unsaturated ketone (VII). Brief treatment of VII with LAH gave the same two alcohols (XII 14%; XIII 86%) but on prolonged treatment the *endo, anti* unsaturated alcohol (XII) was converted to the *endo, anti* saturated alcohol (X). The subsequent reduction of the double bond under these conditions is characteristic of 7-norbornenol derivatives in which the hydroxyl group is *syn* to olefinic link;[26] the epimer in which the hydroxyl is *anti* to the double bond is unaffected under the same conditions. The PMR spectra of XII and XIII provide further confirmation of the configuration of the bridge carbon. In particular, the vinyl signal of XII was observed as a broadened triplet. The broadening may be ascribed to a small stereospecific coupling between the vinyl protons and the C-8 bridge proton which is *anti* to the vinyl protons.[27] In contrast, the vinyl signal of the epimer XIII appears as a sharp well resolved triplet.

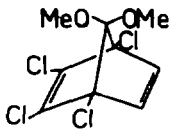
At the inception of this work several *exo* fused 8-substituted tricyclo[3.2.1.$0^{2,4}$] octane derivatives had been reported.[3] However, in view of the simplicity of obtaining the *endo* fused derivatives from the ketal (II), it was tempting to explore the possibility of obtaining the *exo* fused derivatives from the corresponding *exo* ketal (XIV). The precursor (XIV) was obtained, albeit in extremely low yield, by photolytic decomposition of diazomethane in the presence of the norbornadiene derivative (XV).[28] Despite considerable effort, the yield of XIV could not be improved and attempts to prepare compounds of the *exo* series from this ketal were abandoned. Assignment of the *exo* configuration to the ketal (XIV) follows from a comparison of its PMR spectrum with that of the *endo* isomer (II). The spectral parameters* for

TABLE 1. CALCULATED CHEMICAL SHIFTS (PPM) AND COUPLING CONSTANTS (Hz) FOR THE *endo* (II) AND *exo* (XIV) TETRACHLOROKETALS.

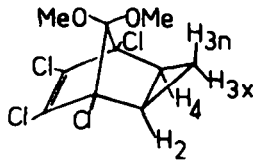
	XIV	II
H_{3n}	6·80	9·58
H_{3x}	8·71	9·08
$H_2(H_4)$	8·10	8·21
$J_{H_{3n}H_{3x}}$	7·00	7·68
$J_{H_{3n}H_2(H_4)}$	3·55	3·62
$J_{H_{3x}H_2(H_4)}$	7·54	7·28

the two isomers are summarized in Table 1. The large steric deshielding experienced by H_{3n} in isomer (XIV) is characteristic of tricyclo[3.2.1.$0^{2,4}$]octanes which have a 9-substituent (OH or OH derivative) *syn* disposed to an *exo* fused cyclopropane ring.[29]

* These parameters were obtained by matching of the experimental spectra to computed spectra; unpublished results of R. I. Kagi.

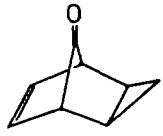


XV

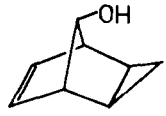


XIV

The *exo* unsaturated ketone (XVI) was prepared by oxidation of the known[3] *exo* alcohol (XVII) or more conveniently by oxidation of a mixture of XVII and its *endo* isomer XIII, since in the latter case the *endo* unsaturated ketone (VII) formed, spontaneously decarbonylates to give tropilidene. The vinyl triplet in the PMR spectrum of XVI was centred at τ 3·18, i.e. downfield from that of norbornenone (τ 3·50).

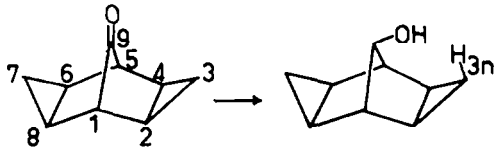


XVI



XVII

The reported reaction of 7-norbornadienyl acetate with diazomethane to give (after reduction with LAH) the alcohols (XVII and XIII) also yields a diadduct alcohol.[3] At the time the stereochemistry of this alcohol (and its acetate) was unknown and furthermore some doubt existed as to the origin of an extraneous (presumably) signal at τ 8·03 in the PMR spectrum of the diadduct alcohol (τ 8·5 in the corresponding acetate). Quite remarkably, integration of this signal indicated one proton. In an effort to resolve these questions we oxidized the crude diadduct alcohol to the corresponding ketone. The liquid ketone* was homogeneous by VPC and showed IR absorption at 1850 and 1775 cm^{-1}. The PMR spectrum of the ketone, Fig. 1, uniquely defines the structure as the *exo, exo* configuration (XIX); the general appearance of the pattern due to the cyclopropane protons is reminiscent of a tricyclo[3.2.1.0^{2,4}]octane suggesting equivalence of the two cyclopropane rings. Lack of coupling between the bridgehead protons (H_1,H_5) and the tertiary cyclopropane protons (H_2,H_4,H_5,H_6) clearly establishes the *exo,exo* configuration.[29]

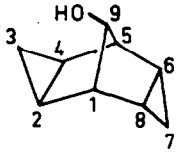


XIX XX

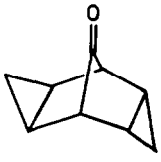
* The ketone is probably identical to the compound described briefly in Ref. 20, footnote 10.

Further evidence for the *exo* configuration (of at least one cyclopropane ring) was obtained from the corresponding alcohol (XX) resulting from LAH reduction of XIX. The PMR spectrum of the alcohol (XX) integrated for five protons in the τ 8·80 region (not six as originally reported[3]) and the multiplet at τ 8·03(doublet of triplets; $J_{H_{3n}H_{3x}} = 5{\cdot}5$, $J_{H_{3n}H_2(H_4)} = 3{\cdot}3$ Hz) we have assigned to H_{3_n} which is sterically deshielded by the proximate OH group.[29]

The configurational assignments for XIX and XX were confirmed by preparation of the corresponding *exo, endo* isomers XXII and XXI. Simmons-Smith reaction on a mixture of the unsaturated tricyclic alcohols XII and XIII resulted in almost complete cyclopropanation of epimer XII whereas the epimer XIII was virtually unreacted. The resulting tetracyclic alcohol* displayed PMR and IR spectra consistent with structure XXI. The sterically deshielded proton H_{3_n} occurred at τ 8·50 in the PMR spectrum and the signal due to this proton approximated the X part of an AM_2X spectrum. Oxidation of the alcohol XXI with Jones reagent furnished the bridged tetracyclic ketone XXII. The PMR spectrum of this ketone was far less



XXI



XXII

symmetrical than that of the *exo, exo* isomer and we feel that even a qualitative comparison of these two spectra leaves very little doubt as to the respective configurations of the two isomeric ketones.

PMR spectra

Several correlations between PMR spectral parameters and configuration of tricyclo[3.2.1.$0^{2,4}$]octane derivatives have been observed in the past and emphasis has been placed on these correlations during structural assignments. Perhaps the most widely used of these correlations is that which relates the configuration of the cyclopropane ring to the chemical shift of the vinyl protons of tricyclo[3.2.1.$0^{2,4}$] oct-6-ene derivatives. The two parent olefins, *exo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene[30] (XXIII) and *endo*-tricyclo[3.2.$10^{2,4}$]oct-6-ene[14] (I) have their vinyl signals at τ 3·71 and 4·37 respectively. The structure of these two tricyclic olefins have been unequivocally determined.† Following this, Sauers[24a] noted that the two monoadducts, XXIV and XXV, arising from reaction between ethyl diazoacetate and norbornadiene

* The product mixture obtained from the Simmons–Smith reaction contained at least one other component. Preliminary investigations indicate that this component is probably a tetracyclic alcohol formally derived from XII by rearrangement then cyclopropanation or the reverse.

† W. von E. Doering and W. Grimme, unpublished results, cited in Ref. 4.

have their vinyl resonances at 3·61 (XXIV) and 4·19 (XXV). In this instance the structure of the *exo* adduct XXIV was confirmed by independent synthesis.

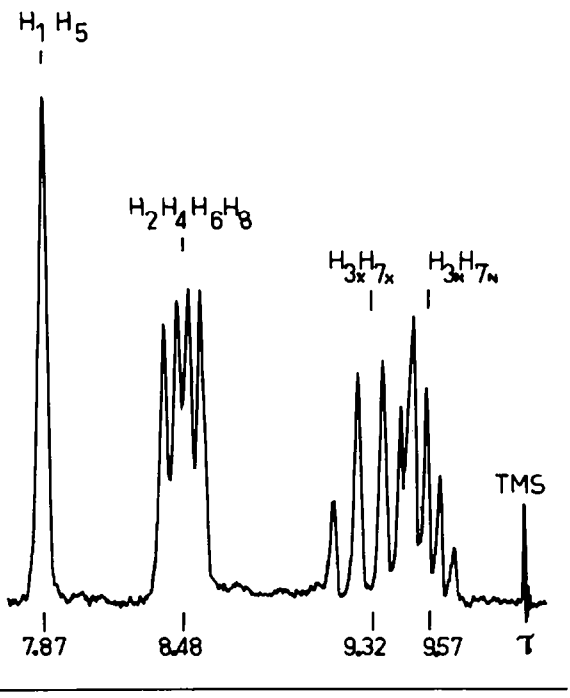


FIG. 1

With the aid of several other examples Pincock[3] was able to add some generality to the correlation: the vinyl protons of *exo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene derivatives are deshielded relative to the vinyl protons of the corresponding norbornene derivatives whereas the vinyl protons of the *endo* isomers are shielded. Examples from the literature and from the present work are collected in Table 2. Without exception, the vinyl resonances of the *exo* isomer are downfield by some 0·3 to 0·5 ppm relative to the vinyl resonances of the corresponding norbornene. The vinyl resonances of the *endo* isomer are uniformly upfield by some 0·1 to 0·4 ppm. The chemical shift difference between the vinyl resonance of the *exo* olefin and its *endo* isomer fall in the range of 0·6 to 0·7 ppm. These long range shielding and deshielding effects have been attributed[3] to the magnetic anisotropy of the cyclopropane ring.[31]

The magnetic anisotropy of the cyclopropane ring is also evidenced in the chemical shift data of the bridge hydrogens at C-8 of both *syn* and *anti* 8-monosubstituted tricyclo[3.2.1.0^{2,4}]octane derivatives[3] (Table 2). When the cyclopropane ring is *exo* the bridge proton at C-8 is nearer to the centre of the cyclopropane ring and is consequently shielded by some 0·1 to 0·3 ppm relative to the bridge proton in the corresponding 7-norbornenyl (or norbornyl) derivative. When the cyclopropane ring

TABLE 2. [a]REFER TO CCl_4 SOLN. [b]IN PPM RELATIVE TO THE CORRESPONDING PROTONS IN THE ANALOGOUS BICYCLO[2.2.1]HEPTANE DERIVATIVES. [c]THIS TRICYCLIC ALCOHOL HAS RECENTLY BEEN SYNTHESIZED IN OUR LABORATORIES; B. C. HENSHAW AND B. L. JOHNSON, IN PRESS.

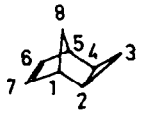
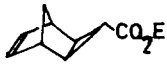
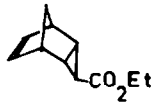
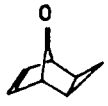
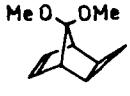
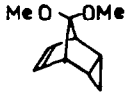
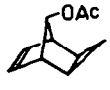
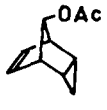
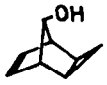
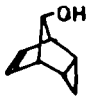
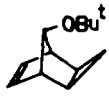
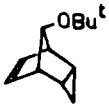
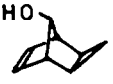
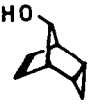
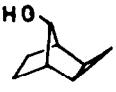
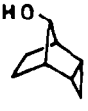
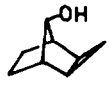
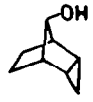
No	Compound	Chem. shift[a] τ H_6H_7	H_8	Chem. shift diff.[b] H_6H_7	H_8	Ref.
XXIII		3.71		−0.36		30
I		4.37		0.30		14,15
XXIV		3.61		−0.46		24a
XXV		4.19		0.12		24a
XVI		3.18		−0.32		This work
VII		3.93		0.43		This work
XVIII		Not known				
IV		4.37		0.35		This work
XXVI		3.58	6.05	−0.39	0.28	3
XXVII		4.28	5.58	0.31	−0.19	3

TABLE 2.—*contd.*

No	Compound	Chem. shift[a] τ H_6 H_7	H_8	Chem. shift diff.[b] H_6 H_7	H_8	Ref.
XVII		3.74	6.68	−0.33	0.13	3
XIII		4.38	6.15	0.31	−0.40	3
XXVIII		3.69	7.07	−0.38	0.33	24b
XXIX		4.39	6.31	0.32	−0.43	24b
XXXI		3.68	6.38	−0.32	0.0	c
XII		4.19	6.07	0.19	−0.31	This work
XXXII			6.47		0.36	3
X			5.98		−0.13	This work
XXX			6.55		0.44	3
XI			5.87		−0.24	This work

is *endo* the bridge proton is nearer to the plane of the cyclopropane ring and therefore experience a deshielding of some 0·2 to 0·4 ppm. The unsaturated alcohol XXXI is exceptional in this regard since the carbinol methine proton at C-8 has the same chemical shift as the analogous proton in *syn*-7-norbornenol.

The configuration at C-7 in 7-monosubstituted norbornenes,[32] norbornadienes[32] and benzonorbornadienes[27] may be assigned from appearances of the vinyl triplet in the PMR spectra. The presence of a small stereospecific coupling between the vinyl protons and the C-7 proton *anti* to the double bond gives rise to a broadening of the usual vinyl "triplet" in the PMR spectrum of the *syn*-7-monosubstituted epimer. In certain instances this stereospecific coupling is resolved and the vinyl signal appears as a doublet of triplets. In contrast, the vinyl signal of the corresponding *anti*-7-monosubstituted epimer is observed as a clean triplet. Extrapolation of these observations to 8-monosubstituted tricyclo[3.2.1.$0^{2,4}$]oct-6-enes would appear to be without objection so that one might expect a broadening of the vinyl triplet in the epimer which has the 8-substituent *anti* to the cyclopropane ring whereas the epimer in which the 8-substituent is *syn* to the cyclopropane ring would be expected to show a clean vinyl triplet. In fact, these expectations have been applied in two instances.

The two monoadducts, XXVI and XXVII, resulting from copper catalysed reaction of diazomethane with 7-norbornadienyl acetate[3] and the two monoadducts, XXVIII and XXIX, arising from Simmons–Smith reaction on 7-norbornadienyl *t*-butyl ether[24b] were each assigned the configuration with the C-8 substituent *syn* to the cyclopropane ring since in each of the four compounds the vinyl signal was observed as a clean triplet. It would appear therefore that the expectation is in part true. However, at the time, no examples of an *anti*-8-monosubstituted tricyclo[3.2.1.$0^{2,4}$] oct-6-ene had been reported and positive evidence for the presence of H-8 to H-6, H-7 coupling was not available. Since then, *endo*, *anti*-tricyclo[3.2.1.$0^{2,4}$]oct-6-en-8-ol (XII) has been reported[1] and the broadening present in the "vinyl triplet" of this compound was commented upon in the previous section. The PMR signal due to the vinyl protons in the *exo*, *anti* isomer XXXI appears as a partially resolved multiplet ($W_{\frac{1}{2}h}$ = 5 Hz).

The PMR spectra of a series of *exo*, *anti*-8-substituted derivatives of benztricyclo [3.2.1.$0^{2,4}$]octene have been examined.[29] The fixed boat-like conformation of these derivatives brings one cyclopropane proton (H_{3n}) into close proximity with the *anti*-8-oxygen function and results in a large steric deshielding of the H_{3n} cyclopropane proton. Furthermore, it was suggested that this deshielding effect could be used in assignment of configuration in 8-substituted tricyclo[3.2.1.$0^{2,4}$]octanes. Several *exo*, *syn*-8-substituted tricyclo[3.2.1.$0^{2,4}$]octanes which possess this fixed boat-like structural feature have been reported.[3,24b] Unfortunately, in one of these reports[24b] the complete PMR spectrum was not given and in any event assignment may have been difficult since the compound was mixed with an isomer. In the second publication,[3] the PMR data are listed and there would appear to be no evidence suggesting steric deshielding of the H_{3n} proton. The PMR spectra of the three compounds in question, *exo*, *syn*-tricyclo[3.2.1.$0^{2,4}$]oct-6-en-8-ol XVII, its acetate XXVI and *exo*, *syn*-tricyclo[3.2.1.$0^{2,4}$]octan-8-ol XXX, have therefore been re-examined.

The *exo*, *syn* acetate XXVI has at best been obtained as a mixture with the *endo*,

syn isomer XXVII but apart from the PMR signal due to highfield cyclopropyl protons the signals are well separated and amenable to assignment. In contrast to the original assignments we believe that the signal at τ 7·65 to be due not to the bridgehead protons of the *endo, syn* acetate XXVII but rather to the sterically deshielded H_{3n} proton of the *exo, syn* acetate XXVI. Relative intensities of the signals support this and also suggest the resonance of the bridgehead protons of the *endo, syn* acetate XXVII are coincident with the resonance signal due to the bridgehead protons of the *exo, syn* acetate XXVI at τ 7·1. Support for these conclusions was obtained from an examination of the PMR spectra of homogeneous samples of each acetate prepared by acetylation of the corresponding alcohols XIII and XVII. The PMR data are presented in the experimental section.

Similarly the other two *exo, syn* derivatives XVII and XXX showed PMR signals which may be ascribed to the sterically deshielded H_{3n} protons. For the *exo, syn* unsaturated alcohol XVII the PMR signal at τ 7·18, originally assigned to the two bridgehead protons, was found to integrate for three protons and correspondingly the highfield multiplet integrated for only three protons. Unfortunately, the signal due to H_{3n} at τ 7·18 was only partially separated from the signal arising from the two bridgehead protons and further analysis was not possible. The PMR spectrum of the *exo, syn* saturated alcohol XXX integrated for only two protons under the signal at τ 9·2 and not three as originally recorded.[3] This signal appears as a doublet of doublets and approximates the M_2 part of an AM_2X type spectrum and may be assigned to the two equivalent tertiary cyclopropyl protons H_2 and H_4. The X part of this pattern is ascribed to the one proton, doublet of triplets at τ 10·1 which must be due to H_{3_x} because of the relatively large cyclopropane *cis* vicinal coupling constant ($J_{H_{3x}H_{2(H_4)}} = 7$ Hz; $J_{H_{3x}H_{3n}} = 6$ Hz). The remaining cyclopropyl proton H_{3n}, which has a relatively small cyclopropane *trans* vicinal coupling constant ($J_{H_{3n}H_{2(H_4)}} = 3$ Hz). resonates further downfield and is included in the multiplet at τ 8·3 to 9·0 which integrates for five protons (2 × H_6, 2 × H_7, H_{3n}) and not four as originally implied.[3] Thus it appears that these three *exo, syn*-8-substituted tricyclo [3.2.1.0^{2,4}]octane derivatives do in fact exemplify steric deshielding of the H_{3n} proton by the 8-oxygen function. Three other examples, XIV, XX, and XXI were discussed in the previous section.

For the sake of completion, mention should also be made of the recent demonstration[33] of the presence of a small but significant stereospecific long range coupling in *endo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene (I) between the *exo* cyclopropyl methylene proton (H_{3x}) and the bridge proton (H_{8a}) *anti* to the cyclopropane ring. The existence of this coupling also promises to be of value in structural analysis of suitably substituted tricyclo[3.2.1.0^{2,4}]octanes.

EXPERIMENTAL

All m.ps and b.ps were uncorrected. Microanalyses were performed at the Australian Microanalytical Service, Melbourne. PMR spectra refer to CCl_4 solutions and were recorded using a Varian A-60 spectrometer. Chemical shifts were measured on the τ-scale relative to internal TMS. Relative areas of signals are shown in brackets. Multiplicities of signals are abbreviated as follows: s = singlet, d = doublet, tr = triplet, etc. IR spectra refer to CCl_4 solutions, unless stated otherwise, and were recorded with a Perkin–Elmer 337 spectrophotometer. Preparative vapour phase chromatography was carried out using an Aerograph 700 Autoprep. with the following column:

0·25 in O.D. × 10 ft aluminium column packed with 15% Ucon 50-HB-2000 on non acid washed Chromosorb W 60/80.

1,2,3,4-*Tetrachloro*-5,5-*dimethoxycyclopenta*-1,3-*diene*. This was synthesized from hexachlorocyclopentadiene and NaOMe–MeOH using the procedure of Yates and Eaton.[34] Distillation of the crude material gave a yellow liquid (85% yield), b.p. 78–82°/0·1 mm. (lit.[35] 108–110°/11 mm). PMR spectroscopy showed the main signal at τ 6·63 with an impurity signal at τ 5·76. Assuming the impurity signal was due to the trimethoxy product, the distilled liquid was calculated to be 93% of the dimethoxy compound.

1,5,6,7-*Tetrachloro*-8,8-*dimethoxy*-endo-*tricyclo*[3.2.1.0^{2,4}]*oct*-6-*ene* (II). The tetrachlorodimethoxycyclopentadiene (20 g) was dissolved in pet. ether (200 ml) and the soln maintained at 0°. Cyclopropene, generated by the method of Closs,[15] was bubbled through the soln, with the aid of a slow N_2 flow, for 10 hr. Depending on the efficiency of the cyclopropene generator this time varied. However, the progress of the reaction could be conveniently monitored by PMR spectroscopy. Evaporation of the solvent under reduced press gave an oil from which the crude product crystallized. The crystals were collected and crystallized from MeOH to give II (60% yield), m.p. 69·5–70·0° (lit.[2] 70–71°). (Found: C, 39·36; H, 3·34. Calc. for $C_{10}H_{10}O_2Cl_4$: C, 39·45; H, 3·29%); PMR: 6·37, s (2·95); 6·49, s (2·95); 8·21, d of d (1·83); 9·08, d of tr (1·20); 9·58, d of tr (1·03).

8,8-*Dimethoxy*-endo-*tricyclo*[3.2.1.0^{2,4}]*octane* (III). Compound II (1·0 g) was dissolved in a mixture of THF (25 ml) and *t*-BuOH (4 ml). The system was purged with N_2 and Li (0·7 g), which had been hammered into plates, was added and the mixture refluxed for 1·5 hr. The excess Li was removed by decantation and the soln was poured into water (250 ml). The product was extracted into pentane (3 × 70 ml) and the pentane extract washed with water (3 × 40 ml) and dried (Na_2SO_4). The residue obtained after evaporation of the solvent was distilled under vacuum (10 mm) to give III (0·30 g; 55%) as a colourless liquid. (Found: C, 71·44; H, 9·34. Calc. for $C_{10}H_{16}O_2$: C, 71·39; H, 9·59%); PMR: 6·76, s (3·01); 6·85, s (3·01); 7·94, m (2·01); 8·1 to 9·5, complex m (7·97). IR: 3065, 3025, 3020, 1032 cm^{-1}.

8,8-*Dimethoxy*-endo-*tricyclo*[3.2.1.0^{2,4}]*oct*-6-*ene* (IV). Compound II (5·0 g) was dissolved in a mixture of THF (65 ml) and t-BuOH (10 ml). The system was purged with N_2 and freshly cut Na (8·7 g) was added. The mixture was stirred and refluxed for 22 hr. The excess Na was removed by decantation and the soln poured into water (750 ml). The aqueous mixture was extracted with isopentane (3 × 100 ml) and the isopentane soln washed with water (2 × 100 ml) and dried (Na_2SO_4). Evaporation of the solvent and distillation of the residue gave IV (76% yield) b.p. 57–58°/2 mm. (Found: C, 72·10, H, 8·61. Calc. for $C_{10}H_{14}O_2$: C, 72·26; H, 8·49%); PMR: 4·38, tr (1·99); 6·84, s (3·05); 6·89, s (3·05); 7·25, p (1·91); 8·5 to 8·9, m (2·09); 9·2 to 9·7, m (2·04). IR: 3055, 3040, 1040, 662, 682, 712 cm^{-1}.

1,5,6,7-*Tetrachloro*-endo-*tricyclo*[3.2.1.0^{2,4}]*oct*-6-*en*-8-*one* (V). Conc H_2SO_4 (25 ml) was cooled to −10° and then added to a soln of II (5·0 g) in benzene (50 ml) in a separating funnel at 5°. The mixture was shaken vigorously for 4 min and then run slowly into ice water (100 g). This mixture was partially neutralized by cautious addition of solid $NaHCO_3$ (21 g), then extracted with CH_2Cl_2 (4 × 100 ml). The CH_2Cl_2 soln was washed with water (1 × 75 ml), dried ($MgSO_4$) and then concentrated to about 15 ml when colourless crystals separated. Separation of the crystals and recrystallization from ether gave V (3·5 g; 82%), m.p. 94–95° dec (lit.[2] 107–108° frothing). (Found: C, 37·46, H, 1·88. Calc. for $C_8H_4OCl_4$: C, 37·20; H, 1·55%); PMR: 8·11, d of d (2·09); 8·85, d of tr (1·05); 9·70, d of tr (0·86); IR: 3060, 1855, 1835, 1800, 1045 cm^{-1}.

Decarbonylation of 1,5,6,7-*tetrachloro*-endo-*tricyclo*[3.2.1.0^{2,4}]*oct*-6-*en*-8-*one* (V). A saturated soln (ca. 2M) of V in diglyme containing benzene as a PMR integration standard was sealed in an NMR tube and maintained at 41·5 ± 0·1°. The progress of the reaction was monitored by chilling the reaction at appropriate time intervals and integration of the vinyl triplet at τ 3·90 due to the product. The PMR integrations were performed with a low temp probe at −20°. Within experimental error the decarbonylation ($t_{\frac{1}{2}}$ = 2·30 hr) was quantitative. On a preparative scale, the tetrachloroketone (neat) was sealed in an ampoule and kept at 100° for ½ hr. Vacuum distillation of the crude product gave a clear liquid which solidified on standing, m.p. 64·5–65·5°. (Found: C, 36·52; H, 1·74. Calc. for $C_7H_3Cl_4$: C, 36·70; H, 1·88%). The PMR spectrum was identical to that reported.[2]

endo-*Tricyclo*[3.2.1.0^{2,4}]*octan*-8-*one* (VI). Compound III (0·19 g) was dissolved in a mixture of THF (2·5 ml) and 3M aqueous perchloric acid (1·2 ml) and the soln allowed to stand at room temp for 3 hr. Water (100 ml) was added and this aqueous mixture extracted with isopentane (3 × 60 ml). The isopentane soln was washed with water (2 × 50 ml), dried (Na_2SO_4) and the solvent evaporated to give a colourless semi-crystalline residue (0·11 g). Preparative VPC (col. temp 160°) gave VI as very soft crystals, m.p. 65–66° (lit.[1,2] 71–72°, 58–61°). (Found: C, 78·52; H, 8·44. Calc. for $C_8H_{10}O$: C, 78·65; H, 8·25%); PMR: 7·79, m (2·00); 8·0 to 9·5, m (8·00); IR: 3065, 3030, 1825, 1780, 1770 cm^{-1}.

On a larger scale the crude ketone was purified directly by crystallization from n-pentane.

endo-*Tricyclo*[3.2.1.0^{2,4}]*oct-6-en-8-one* (VII). Compound IV (2·3 g) in THF (10 ml) was added to a pre-cooled soln of 3M aqueous perchloric acid (20 ml) and THF (30 ml) at −5° and the resulting mixture kept at −15° for 4 hr. The soln was neutralized with solid $NaHCO_3$ and then extracted with ether (4 × 100 ml). The ethereal soln was washed with sat Na_2CO_3 aq (1 × 50 ml), water (1 × 50 ml) and dried ($MgSO_4$). The solvent was evaporated under reduced press at 0° to yield a solid which after crystallization (3 times) from cold n-pentane gave VII (0·8 g, 50%), m.p. 30·5–31°, noticeable bubbling at 35° (lit.[1] 32–32·5°). Since this ketone undergoes facile decarbonylation no microanalytical data was obtained. PMR: 3·93, tr (2·00); 6·83, p (2·00); 8·47, m (2·12); 9·09, d of tr (0·96); 9·62, d of tr (0·92). First-order analysis gave $J_{H_{3x}H_{3n}} = J_{H_{3x}H_2(H_4)} = 7$ and $J_{H_{3n}H_2(H_4)} = 4$ Hz. IR: 3065, 3045, 3015, 1860, 1820, 1780, 1040, 692, 646, 604 cm^{-1}.

Decarbonylation of endo-*tricyclo*[3.2.1.0^{2,4}]*oct-6-en-8-one* (VII). The progress of this reaction was monitored in the same manner as described above for the tetrachloroketone. At 40·0 ± 0·1° the decarbonylation in diglyme was quantitative ($t_{\frac{1}{2}}$ = 1·13 hr). For preparative purposes the neat ketone was kept at 80° for 15 min. VPC (col. temp 115°) of the crude product showed only one component which was collected and shown to be identical (PMR and IR) to tropilidene.

endo-*Tricyclo*[3.2.1.0^{2,4}]*octan-8-one tosylhydrazone* (VIII). Compound VI (0·16 g) was dissolved in a mixture of EtOH (8 ml) and *p*-toluenesulphonyl hydrazide[36] (0·30 g). The soln was refluxed for 15 min and then the solvent was evaporated under reduced press. The semi-crystalline residue was triturated with MeOH and the resulting solid crystallized from MeOH to give VIII (0·16 g, 42%), m.p. 172–173°, dec (cap.). (Found: C, 61·84; H, 6·41; N, 9·39. Calc. for $C_{15}H_{18}O_2N_2S$: C, 62·04; H, 6·25; N, 9·65%).

Reduction of endo-*tricyclo*[3.2.1.0^{2,4}]*octan-8-one tosylhydrazone* (VIII). Sodium borohydride (0·3 g) was added to a soln of VIII (0·11 g) in dioxane (7 ml). The mixture was refluxed for 50 min during which time the condenser outlet was connected to a liquid air cooled trap. Volatile material in the trap and the condenser was rinsed back into the reaction mixture with isopentane (5 ml). The mixture was diluted with water (20 ml) and the isopentane extract separated. The aqueous phase was extracted with further isopentane (1 × 5 ml) and the combined isopentane extract was washed with water and dried (Na_2SO_4). Preparative VPC (col. temp 90°) gave IX as soft crystals. The product gave IR spectrum and VPC retention time identical to the saturated hydrocarbon described below.

endo-*Tricyclo*[3.2.1.0^{2,4}]*oct-6-ene* (I). This was prepared from cyclopentadiene and cyclopropene using the procedure of Closs and Krantz.[15] The crude product was purified by preparative VPC (col. temp 115°). As collected, the tricyclic olefin, m.p. 30–31° (lit.[15,16] 30–31°, 30–32°) was shown to be >99% one peak on analytical VPC. The PMR spectrum of I was identical with that reported.[14]

endo-*Tricyclo*[3.2.1.0^{2,4}]*octane* (IX). Compound I was hydrogenated with PtO_2 in THF. After uptake of an equimolar amount of H_2 the catalyst was removed and the soln diluted with water. The product was extracted into pentane and the pentane soln was washed with water, dried and partially evaporated. Preparative VPC (col. temp 90°) gave IX. (Found: C, 88·84; H, 11·18. Calc. for C_8H_{12}: C, 88·82; H, 11·18%); IR: 3050, 3005, 2995, 1030 cm^{-1}.

1,2,3,4-*Tetrachloro*-7,7-*dimethoxynorborna*-2,5-*diene* (XV). This was prepared according to Mackenzie.[28] The purified product gave m.p. 53–55° (lit.[28] 54–55°). PMR spectroscopy showed two signals at τ 3·47 and 6·45 in the ratio of 2:6.

1,5,6,7-*Tetrachloro*-8,8-*dimethoxy*-exo-*tricyclo*[3.2.1.0^{2,4}]*oct*-6-*ene* (XIV). Despite considerable experimentation, XV failed to show evidence (PMR) of reaction with diazomethane in the presence of cuprous bromide. The diene XV was also unreactive to Simmons–Smith conditions. Unchanged reactant was isolated in all cases. Photolytic decomposition of diazomethane in the presence of XV gave the desired product in low yield.

The diene XV (8·0 g) was dissolved in an ethereal soln of excess diazomethane. The soln was irradiated with a 100 W globe until the diazomethane colour had disappeared. The solvent was evaporated and the residue chromatographed on neutral alumina(500 g). Elution with pet. ether gave a liquid fraction (0·4 g; 4·8%) which after vacuum distillation gave XIV as a colourless oil. (Found: C, 39·68; H, 3·47. Calc. for $C_{10}H_{10}O_2Cl_4$: C, 39·45; H, 3·29%); PMR: 6·39, s (3·01); 6·53, s (3·01); 6·80, d of tr (0·99); 8·10, m (1·92); 8·7, d of tr (1·07).

exo-*Tricyclo*[3.2.1.0^{2,4}]*oct-6-en-8-one* (XVI). Compound XVII was prepared according to the published procedure.[3] To a soln of this alcohol (1·6 g) in acetone (50 ml), Jones reagent (6 ml) was added all at once. The mixture was swirled for about 20 sec and then poured into water (500 ml). The aqueous mixture was immediately extracted with pentane (3 × 170 ml) and the pentane soln washed with water (1 × 30 ml) and dried. Evaporation of the solvent and preparative VPC (col. temp 120°) of the liquid residue (1·2 g) gave

XVI as a colourless liquid. (Found: C, 79·95; H, 6·71. Calc. for C_8H_8O: C, 79·56; H, 6·95%); PMR: 3·18; tr (1·98), 7·02 partially resolved m (1·98); 8·59 broad q (2·04); 8·89 partially resolved m (2·00); IR 3062, 3036, 1850, 1815, 1790, 1785, 1035, 680, 632, 605 cm^{-1}.

In another run a mixture[3] of XVII and XIII was oxidized under the same conditions. The *exo*-ketone XVI was obtained free of any *endo*-ketone VII since the latter decarbonylates to tropilidene during work up.

Several attempts to obtain the dimethyl ketal of *exo*-tricyclo [3.2.1.$0^{2,4}$]oct-6-en-8-one gave only recovered ketone. Attempts to prepare XVI via MnO_2 oxidation of XVII gave only tropilidene. Presumable the MnO_2 functions as a very efficient catalyst for decarbonylation of XVI.*

endo, anti- *and* endo, syn-*Tricyclo*[3.2.1.$0^{2,4}$]*octan*-8-*ols* (X) *and* (XI). A soln of VI (12 g) in MeOH (100 ml) was added dropwise over a period of 15 min to a stirred mixture of $NaBH_4$ (9·0 g) and MeOH (60 ml) at 0°. After the addition was complete, the mixture was stirred for an additional 3 hr at room temp. The reaction mixture was stirred with sat NH_4Cl aq and then extracted with ether (5 × 200 ml). The ethereal soln was washed with water (2 × 100 ml), dried ($MgSO_4$), and then evaporated to yield a white solid. VPC of the crude product showed the presence of two alcohols (1:1). The alcohols were separated by preparative VPC (col. temp 140°). Compound X after crystallization from n-pentane gave m.p. 138·5–139° (lit.[1,2] 136–138°, 137–139°). (Found: C, 76·96; H, 9·72. Calc. for $C_8H_{12}O$: C, 77·35; H, 9·74%); PMR: 5·98, broad s (0·92); 7·10, s (0·98); 7·97, m (1·96); 8·1 to 9·6, broad band (8·14); IR: 3630, 3070, 3030, 3008, 1070, 1055, 1040 cm^{-1}. Compound XI after crystallization from n-pentane gave m.p. 131–131·5° (lit.[1,2,3] 128–130°, 125–127°). The PMR spectrum was identical with that reported.[3] IR: 3630, 3595, 3075, 3020, 3010, 1070, 1055, 1045, 1040 cm^{-1}.

Reduction of VI with LAH in ether gave the epimeric X and XI in the ratio 33:67.

endo, anti- *and* endo, syn-*Tricyclo*[3.2.1.$0^{2,4}$]*oct*-6-*en*-8-*ols* (XII) *and* (XIII). Compound VII (0·65 g) was dissolved in MeOH (30 ml) and this soln was added dropwise to a magnetically stirred suspension of $NaBH_4$ (2 g) in MeOH (20 ml) at 0°. The mixture was stirred for a further 3 hr at 0° and for 1 hr at room temp and then decomposed with sat NH_4Cl aq. The product was extracted into ether (4 × 100 ml) and the ethereal soln washed with water (2 × 100 ml) and dried ($MgSO_4$). Evaporation of the solvent gave an oil which by VPC analysis consisted of two components (XII and XIII in the ratio 25:75). The two components were separated by preparative VPC (col. temp 140°). The *endo, syn* alcohol XIII was crystallized from n-pentane, m.p. 63–65° (lit.[3] 60–62°). The PMR spectrum was identical to that reported.[3] IR: 3630, 3590, 3060, 3020, 1045, 865, 670 cm^{-1}. VPC collection of the *endo, anti* unsaturated alcohol XII was comparatively inefficient since this isomer was volatile and hygroscopic. After collection the crude solid was sublimed (once) at atm press to give an analytical sample† of XII, m.p. 75–76°. (Found: C, 78·42; H, 8·32, Calc. for $C_8H_{10}O$: C, 78·65; H, 8·25%); PMR: 4·19, broad partially resolved tr (2·08); 6·07, broad s (0·95); 7·10, broad p (2·08); 7·32, s (0·98); 8·73, m (1·96); 9·73, m (1·96). IR: 3625, 3575, 3065, 3035, 1045, 655 cm^{-1}.

LAH reduction of VII at 0° gave the same two alcohols: (XII; 14% and XIII; 86%). Reduction with LAH at room temp for 3 hr gave a mixture of X (14%) and XIII (86%).

exo,exo-*Tetracyclo*[3.2.1.$0^{2,4}0^{6,8}$]*nonan*-9-*one* (XIX). A mixture of XVII and XII and the diadduct alcohol was prepared according to the published procedure[3] except that excess diazomethane was used in order to optimize the proportion of diadduct alcohol. The mixture was oxidized in the same manner as described above for the preparation of XVI. Preparative VPC (col. temp 150°) gave XIX (30% yield based on 7-norbornadienyl acetate) as a clear liquid. (Found: C, 80·36; H, 7·62. Calc. for $C_9H_{10}O$: C, 80·56; H, 7·51%); PMR: 7·87, s, $W_{\frac{1}{2}h}$ = 2·5 Hz (1·99); 8·48, d of d (3·98); 9·32, d of tr, and 9·57, d of tr (combined relative area = 4·01). First order analysis gave $J_{H_{3n}H_{3x}} = J_{H_{7n}H_{7x}} = 7$, $J_{H_{3n}H_2(H_4)} = J_{H_{7n}H_6(H_8)} = 4$ and $J_{H_{3x}H_2(H_4)} = J_{H_{7x}H_6(H_8)} = 7$ Hz; IR: 3060, 3025, 1850, 1775, 1040 cm^{-1}.

exo,exo-*Tetracyclo*[3.3.1.$0^{2,4}.0^{6,8}$]*nonan*-9-*ol* (XX). A mixture of XIX (430 mg), ether (40 ml) and LAH (700 mg) was refluxed for ½ hr. After decomposition with sat Na_2SO_4 aq, the reaction mixture was extracted with ether (3 × 60 ml). The ethereal soln was washed with water (1 × 60 ml), dried (Na_2SO_4) and evaporated to yield a crystalline solid (410 mg) which after crystallization (twice) from n-pentane gave XX, m.p. 60–61° (lit.[3] 6163). (Found: C, 79·22; H, 8·66. Calc. for $C_9H_{12}O$: C, 79·37; H, 8·88%); PMR: 6·72, broad

* Analogous results have been obtained with MnO_2 oxidation of the bridge alcohol of 1,6-methanocyclodecapentaene.[3,7] In this instance, however, the intermediate ketone is apparently too unstable to be obtained by alternative oxidative methods.

† The analytical sample was obtained in these laboratories by Bruce C. Henshaw.

s, $W_{\frac{1}{2}h}$ = 5 Hz (0·97); 7·53, sharp s, OH (1·02); 7·76, s, $W_{\frac{1}{2}h}$ = 3 Hz (2·03); 8·03, d of tr (0·97); 8·90, m (5·06); 9·70, d of tr (1·94); IR: 3620, 3610 (sh), 3060, 1110, 1040 cm^{-1}.

Preparation of exo, endo-*tetracyclo*[3.3.1.0^{2,4}.0^{6,8}]*nonan*-syn-9-*ol* (XXI). A mixture of XII and XIII, (8·0 g) obtained by Li ammonia reduction* of VII, was dissolved in anhyd ether (150 ml). Zn Cu couple[38] (30 g) was added and the mixture stirred whilst CH_2I_2 was added during 15 min. After the initial reaction had subsided the mixture was refluxed for a further 11 hr. Isolation in the usual manner afforded a dark coloured oil (8·5 g) which was distilled under vacuum. The distillate was dissolved in n-pentane (30 ml) and then washed with $AgNO_3$ aq (5 × 20 ml), water (2 × 20 ml) and dried (Na_2SO_4). Evaporation of the solvent gave an oil (1·85 g) which was chromatographed on 10% $AgNO_3$–Woelm basic alumina (100 g). Elution with 10% ether in pentane gave a solid fraction which after crystallization from n-pentane yielded XXI (130 mg), m.p. 81·5–82°. (Found: C, 79·48; H, 8·85. Calc. for $C_9H_{12}O$: C, 79·37; H, 8·88%); PMR: 6·34, broad s (0·97); 7·00, s, OH (0·97); 7·78 broad s, $W_{\frac{1}{2}h}$ = 6 Hz (1·94); 8·50, d of tr, J_{gem} = 5, J_{vic} = 3·5 Hz (1·00); 8·65 to 9·25, m (3·11); 9·25 to 10·2, m (4·02); IR: 3630, 3075, 3025, 3010, 1070, 1050 cm^{-1}.

The aqueous $AgNO_3$ washings after decomposition with conc NH_4OH gave a solid (3·1 g) which by PMR spectroscopy was shown to be a mixture of, XIII (ca. 90%) and, XII (ca. 10%).

Preparation of exo, endo-*tetracyclo*[3.3.1.0^{2,4}: O^{6,8}]*nonan*-9-*one* (XXII). Jones reagent (0·7 ml) was added to a soln of XXI (50 mg) in acetone (15 ml) and the mixture swirled for ca. 20 to 30 sec and then poured into water (150 ml). The aqueous soln was immediately extracted with ether (3 × 50 ml) and the ether extract washed with water (2 × 20 ml) and dried (Na_2SO_4). Evaporation of the ether gave a low melting solid (40 mg) which was crystallized from cold n-pentane to give XXII, m.p. 26–28°. (Found: C, 80·68; H, 7·63. Calc. for $C_9H_{10}O$: C, 80·56; H, 7·51%); PMR: 7·65, broad s, $W_{\frac{1}{2}h}$ = 7 Hz (2·09); 8·5 to 9·9, m (7·91); IR: 3070, 3060, 3035, 3000, 1830, 1775, 1760, 1040, 1035.

PMR spectra of exo, syn-8-*acetoxytricyclo*[3.2.1.0^{2,4}]*oct*-6-*ene* (XXVI) *and* endo, syn-8-*acetoxytricyclo*[3.2.1.0^{2,4}]*oct*-6-*ene* (XXVII). Homogeneous samples of XIII and XVII were prepared according to the published procedure[3] and each alcohol was converted to the corresponding acetate with Ac_2O–pyridine.

PMR: XXVI: 3·58, tr (1·95, vinyl); 6·05, broad s (0·95, CHOAc); 7·05, broad m (1·95, bridgehead); 7·75, m (1·05, H_{3n}); 8·07, s (3·05, CH_3CO); 8·95, m (3·05, remaining cyclopropane protons).
XXVII: 4·28, tr (2·00, vinyl); 5·58, broad s (0·95, CHOAc); 7·15, broad m (1·95, bridgehead); 8·02, s (3·05, CH_3CO); 8·63, m (2·02, two cyclopropane protons); 9·32, m (2·02, two cyclopropane protons).

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* Under certain conditions this method of reduction gives rise to bicyclic alcohols which presumably arise via reductive cleavage of the tricyclic precursors. Details of this will be published later.

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