

## Adamantane Chemistry. Part 3.<sup>1</sup> Abnormal Hypiodite Reactions of 2-Substituted Adamantan-2-ols; Synthetic Routes to 4-Oxahomo- and 2-Oxa-adamantanes, and 7-Substituted-bicyclo[3.3.1]nonan-3-ols

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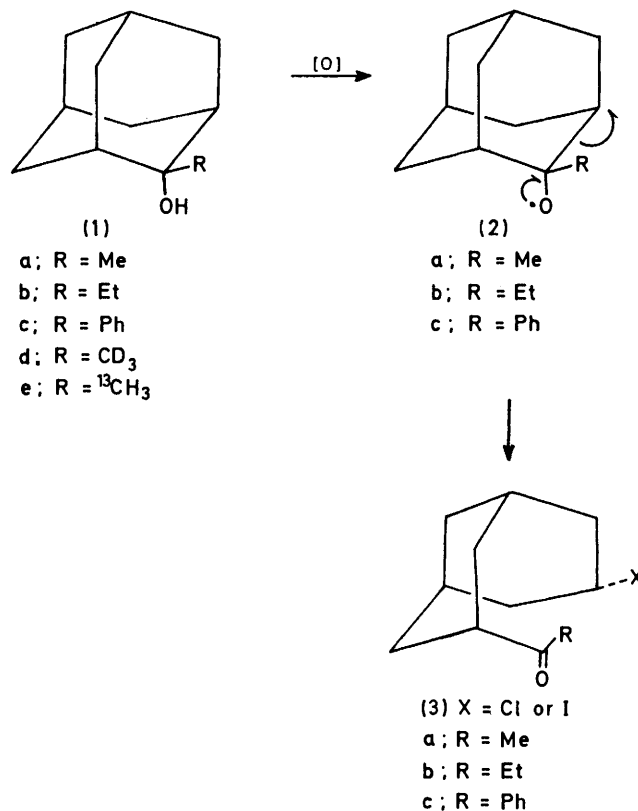
Reaction of 2-methyladamantan-2-ol (1a) with lead tetra-acetate and iodine in boiling benzene did not yield the expected radical fragmentation product (3a), but rather a yellow, crystalline di-iodo-ether which was previously assigned structure (4) on the basis of chemical degradative evidence and on an apparent  $m/e$  418 molecular ion (electron impact). Structure (4) is not supported by the spectroscopic data, and <sup>13</sup>C n.m.r. studies on an isotopically enriched sample of the di-iodo-ether indicate the structure to be (5b). Re-investigation of the mass spectrum has revealed that the (fairly intense) molecular ion has  $m/e$  416; previous assignment of the molecular ion to the  $m/e$  418 peak (*i.e.*  $M + 2$ ) arose largely through the absence at that time of mass-marking facilities and the large interval between  $M^{++}$  and the highest mass fragment ion. Similar hypiodite reaction of 2-ethyl- (1b) and of 2-phenyl-adamantan-2-ol (1c) gave, respectively, the products (5a) and (7b), the latter arising from the hydrolysis during isolation of the iodo-ether (6c). Investigation of the chemistry of (5b) and (7b) has revealed useful preparative routes to substituted 4-oxahomo- and 2-oxa-adamantanes as well as 7-substituted-bicyclo[3.3.1]nonan-3-ols. Several unusual reactions have been discovered, and reaction mechanisms are suggested.

PRELIMINARY investigations of the hypohalite reactions of various adamantanol<sup>2-4</sup> revealed that the courses of the reactions could not be predicted, but were dependent upon both the structures of the alcohols and the nature of the oxidising agents employed. In the case of the tertiary alcohols, *e.g.* (1a—c), it was expected that pyrolytic decomposition of the derived hypohalites would result in the fragmentation of the intermediate t-alkoxyl radicals (2a—c) to give the radical chain transfer products, the  $\omega$ -halogenoketones (3a—c). The alternative mode of reaction, namely intramolecular hydrogen atom abstraction, is not open to the radicals (2a—c) because of the absence of a  $\delta$  H-atom suitably located for involvement in the necessary six-centre cyclic transition state. Conversion of the alcohols (1a—c) to the corresponding hypochlorites (by reaction with Cl<sub>2</sub>O) followed by thermolysis or photolysis (CCl<sub>4</sub> solution) did indeed afford the chloro-ketones (3a—c), and in good yield.<sup>2</sup> However, the related hypiodite reactions were found<sup>3</sup> to proceed in a completely unexpected and novel direction, and the results of this study are detailed here.

**Hypiodite Reactions of the Alcohols (1a—c).**—Reaction of (1a) with lead tetra-acetate and iodine in boiling benzene gave a yellow, crystalline compound of unusually high density. Initial indications (see below) were that it possessed the molecular formula C<sub>11</sub>H<sub>16</sub>I<sub>2</sub>O and was a di-iodo-ether. The compound, hereafter referred to as (X), was acid-labile and its prolonged storage at room temperature also led to decomposition with the evolution of iodine. It was expedient, therefore, to carry out the hypiodite reactions in the presence of a mild base (calcium carbonate), and the weakly basic conditions were maintained during the work-up of the reaction product.

Because the original structure assigned to (X), namely (4),<sup>3,†</sup> was not that anticipated on mechanistic grounds, nor was the structure self-evident from the spectro-

scopic data (see below), attempt was made to determine the structure by X-ray methods. Oscillation and Wissenberg photographs revealed that (X) crystallised in the triclinic system with eight molecules in a unit cell of volume 1440 Å<sup>3</sup>. Because of the large number of



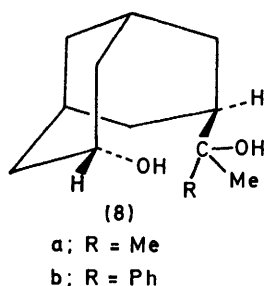
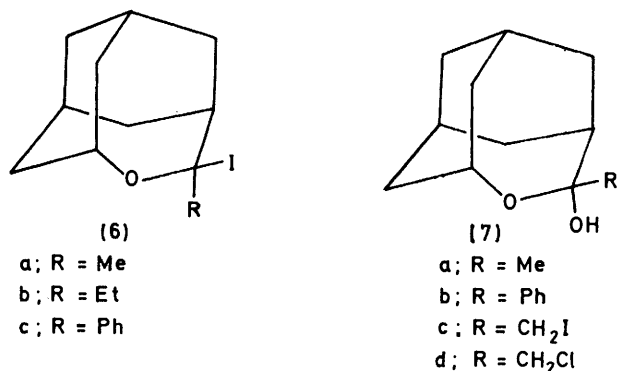
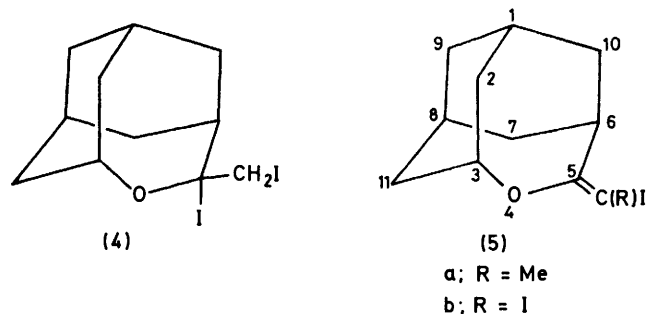
iodine-to-iodine vectors it was considered that the carbon skeleton of the molecule could not be established with sufficient precision to make the collection of diffraction data worthwhile; the X-ray study was therefore abandoned.

All attempts to isolate a di-iodo-ether from the hypo-

† We are indebted to a referee for comments concerning the original manuscript of this paper; additional experimental details (and the regrouping of data) are now included.

iodite reaction of (1b) failed. The crude reaction product exhibited a weak absorption in the i.r. spectrum at  $1635\text{ cm}^{-1}$  and a sharp singlet (3 H) at  $\tau$  7.6 in the  $^1\text{H}$  n.m.r. spectrum. Chromatography on neutral alumina gave the main component, an unstable crystalline compound, which was identified as one of the two geometrical isomers of the olefin (5a) from correlation with some of the degradation products of (X).

The analogous hypoiodite reaction of (1c) gave a



crystalline product identified as the lactol (7b). Confirmation of the structure was obtained by cleavage of (7b) with methylmagnesium iodide to give 1-(3-hydroxybicyclo[3.3.1]nonan-7-yl)-1-phenylethanol (8b).<sup>\*</sup> The iodo-ether (6c) is the likely initial product of the hypoiodite reaction which suffers rapid hydrolysis to (7b) under the aqueous work-up conditions.

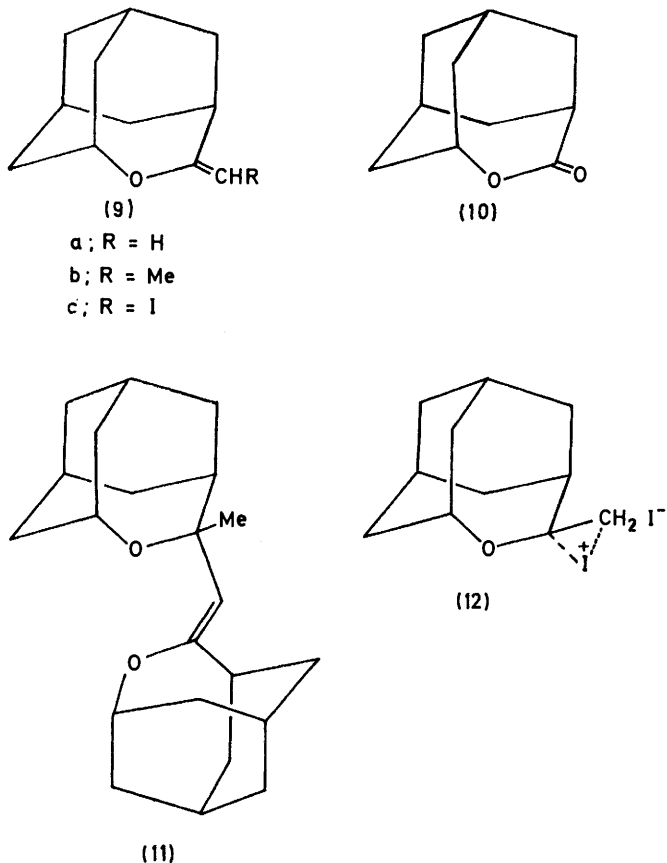
*Chemical Evidence for the Structure of (X).*—Treatment

<sup>\*</sup> No conformational preferences of the bis-*endo*-substituted bicyclo[3.3.1]nonanes should be inferred from the formulae (8), (15), and (16). It seems unlikely, however, that contributions from the dual-chair conformations would be important.

of (X) with  $\text{Bu}^t\text{OK-DMSO}$  afforded a product which was assigned the iodovinyl ether structure (9c) in view of its spectroscopic properties, notably  $\nu_{\text{max}}$   $1612\text{sh cm}^{-1}$  (vinyl ether C=C stretch) and  $\tau$  5.32 (1 H, s, =CH). Indeed, the  $^1\text{H}$  n.m.r. spectrum indicated the presence of only one of the two geometrical isomers, and it seems likely that in (9c) the oxygen and iodine atoms are *trans* to one another.

Treatment of (X) with  $\text{LiAlH}_4$  gave (9c) as the major reaction product. Ozonolysis of (9c) gave only minor amounts of the expected cleavage product, the known lactone (10), as detected by g.l.c.

Reaction of (X) with zinc dust in ether containing acetic acid gave the dimeric compound (11) in nearly quantitative yield. The inference of this result is that  $\beta$ -elimination of iodine (as  $\text{ZnI}_2$ ) occurs from (X) to give the vinyl ether (9a) which dimerised under the acidic conditions of the reaction. Accordingly, structure (4) was assigned to (X); this formulation was subsequently shown to be incorrect. However, other results lent support to structure (4). For example, reaction of (X)



with tri-*n*-butyltin hydride in ether followed by aqueous work-up afforded the lactol (7a) in modest yield. Since vicinal dihalides are known to give olefins [*e.g.* (9a)] with this reagent,<sup>5</sup> the formation of the lactol could be rationalised by the sequence (4)  $\rightarrow$  (9a)  $\rightarrow$  (7a), the last step occurring during the hydrolytic work-up. Hydrogenolysis of (9c) over  $\text{PtO}_2$  catalyst in ethanol,

followed by aqueous work-up, also gave the lactol (7a). However, although vinyl ethers are known to add water readily,<sup>6</sup> it is nevertheless surprising that (7a) was still formed when both the hydrogenation and the work-up were carried out under alkaline conditions, thereby removing the possibility of acid-catalysed hydration.

The structure of the lactol (7a) itself was confirmed unequivocally by cleavage of the C(5)-O ether linkage with methylmagnesium iodide to give *endo*-2-(3-hydroxybicyclo[3.3.1]nonan-7-yl)propan-2-ol (8a), a compound also obtained from reaction of an excess of methylmagnesium iodide with the known lactone (10). Treatment of (10) with one equivalent of the Grignard reagent gave both the lactol (7a) and the diol (8a).

The iodovinyl ether (9c) is readily hydrated when it is isolated by chromatography over silica gel, giving the iodomethyl lactol (7c). The spectroscopic properties of (7c) and of (X) are quite distinct, indicating that the analogous structure (4) cannot be equated with that of (X) in the absence of marked anomalous effects arising from the presence of the two iodine atoms.

The lability of (X) towards acids was also examined. Whereas (X) was relatively stable towards trifluoroacetic acid (very slow liberation of iodine), the addition of a few drops of concentrated hydrochloric acid to a rapidly stirred solution of (X) in chloroform led to the rapid and immediate evolution of iodine. Although the i.r. spectrum of the crude product indicated the presence of vinyl ethers ( $\nu_{\max}$  1 625  $\text{cm}^{-1}$ ) the only product isolated was the chloromethyl lactol (7d) (46%) whose structure has been established unequivocally by X-ray crystallography.<sup>1</sup>

The chemical evidence for the structure of (X) led to the consideration of compounds (4), (5b), and the iodonium ion (12). However, both (4) and (12) were not consistent with all of the data obtained from routine spectroscopic measurements. Additionally, the apparent lack of salt-like character and the lack of reaction of (X) with silver nitrate and potassium carbonate in aqueous dioxan militates further against structure (12). Structure (5b) was ruled out for a long time because of an operator error in the interpretation and measurement of the electron impact mass spectrum. The molecular ion was assigned<sup>3</sup> the mass 417.921 1 which, within experimental error, corresponded to the species  $(\text{C}_{11}\text{H}_{16}\text{I}_2\text{O})^{+\cdot}$ , consistent with structure (4) but not (5b). Later, and more detailed, spectroscopic evidence (see below), showed clearly that the structure could not be (4), and hence the validity of the mass spectrometric result was open to question. Re-analysis of (X) in the original mass spectrometer (AEI MS-901) produced the same answer whereas analysis on a VG-Micromass 7070F instrument (and later on the MS-902) showed clearly that the molecular ion had  $m/e$  416 and that the  $m/e$  418 peak was the isotopic ion  $(M + 2)^{+\cdot}$ . Unlike the VG instrument, the MS-902 did not possess the mass-marking facility. The molecular ion for (X) is relatively intense and it appears that when the AEI mass spectrometer was operated at high resolution the  $(M + 2)$  ion was the one

consistently selected for accurate mass measurement because of its relative strength. The expected value for the mass of the (5b) isotopic species  $(^{12}\text{C}_9^{13}\text{C}_2\text{H}_{14}\text{I}_2\text{O})^{+\cdot}$  is 417.920 1—within 2.5 p.p.m. of the measured value. The mass of the molecular ion could not be deduced from the masses of the fragment ions because the primary fragmentation involves loss of iodine. The large interval between  $m/e$  416 and  $m/e$  289 ( $M^+ - \text{I}$ ) made it impossible to cross-check the mass of the molecular ion with any accuracy. The assumed molecular ion of mass 418 was thought originally to fragment to give the ion 289 by loss of  $\text{H}_2\text{I}$ , a species that is found in the mass spectra of alkyl iodides.

*Spectroscopic Data for (X) [= (5b)].*—The presence of an i.r. absorption band at 1 582  $\text{cm}^{-1}$  ( $\epsilon$  78) can now be assigned to a C=C stretch within the structural unit  $-\text{O}-\text{C}=\text{CI}_2$  rather than to a combination band.<sup>3</sup> The lack of an AB signal in the region  $\tau$  6.2—7.8 in the  $^1\text{H}$  n.m.r. spectrum rules out the presence of a  $\text{CH}_2\text{I}$  grouping [structure (4)]. The hypiodite product obtained from deuteriated 2-methyladamantan-2-ol (1d) had a  $^1\text{H}$  n.m.r. spectrum identical to the product from unlabelled starting material (1a); in the absence of H-D exchange during reaction and product isolation, this result indicates complete hydrogen (deuterium) loss from the methyl group of the adamantanol as a consequence of product formation—a necessary prerequisite in the conversion into (5b). The assignment of the low field resonances at  $\tau$  5.37 (H-3) and 6.15 (H-6) are consistent with structure (5b).

Initially, in view of the known lability of the di-iodo-ether (X) to acid [*cf.* (X)  $\longrightarrow$  (7d), presumably *via* an intermediate vinyl ether or carbonyl compound] and the assumption that it had the constitution  $\text{C}_{11}\text{H}_{16}\text{I}_2\text{O}$ , interpretation of the  $^{13}\text{C}$  spectra ( $\text{CDCl}_3$  solution) proved difficult. The singlet at 165.1 p.p.m. can now be assigned to C(5) in (5b) rather than to a deshielded carbon atom of a product arising from decomposition during the necessarily prolonged time for data acquisition (*n.b.* the hypiodite product is not very soluble). The preparation of (5b) labelled at the exocyclic carbon atom to the extent of 10 atom %  $^{13}\text{C}$  [from 10 atom %  $^{13}\text{C}$ -labelled-(1e)] allowed assignment of the singlet resonance at -10.35 p.p.m. to the  $=\text{CI}_2$  olefinic carbon atom. Also detected in this sample was the coupling  $^3J_{\text{C,H-6}}$  3.9 Hz. The  $^{13}\text{C}$ -enrichment was insufficient to determine the  $^{13}\text{C}=\text{CI}_2$  coupling constant. The assignment of the remaining resonances in the spectra of (5b) are straightforward (see Experimental section) and confirm the symmetry of the molecule, but it should be made clear that the  $^{13}\text{C}$  spectra enabled an accurate proton count to be conducted from the observed intensities and multiplicities, and gave the first clue that the constitution was  $\text{C}_{11}\text{H}_{14}\text{I}_2\text{O}$  and not  $\text{C}_{11}\text{H}_{16}\text{I}_2\text{O}$ .

Finally, the difference in  $^{13}\text{C}$  chemical shifts of the olefinic carbon atoms in the  $\text{OC}=\text{CI}_2$  unit of (5b), a full 175 p.p.m., deserves specific mention. The iodine atoms deshield C(5) but shield the exocyclic carbon atom. The observed chemical shifts are in approximate agreement

with crude calculations based on  $\alpha$ -,  $\beta$ -, and  $\gamma$ -substituent parameters.<sup>7</sup>

*On the Mechanisms of the Hypoiodite Reactions.*—Although the precise mechanisms for the formation of (5b), (5a), and (presumably) of (6c), respectively, from hypoiodite reactions on (1a–c) remain obscure, our results have delineated some of the main mechanistic features.

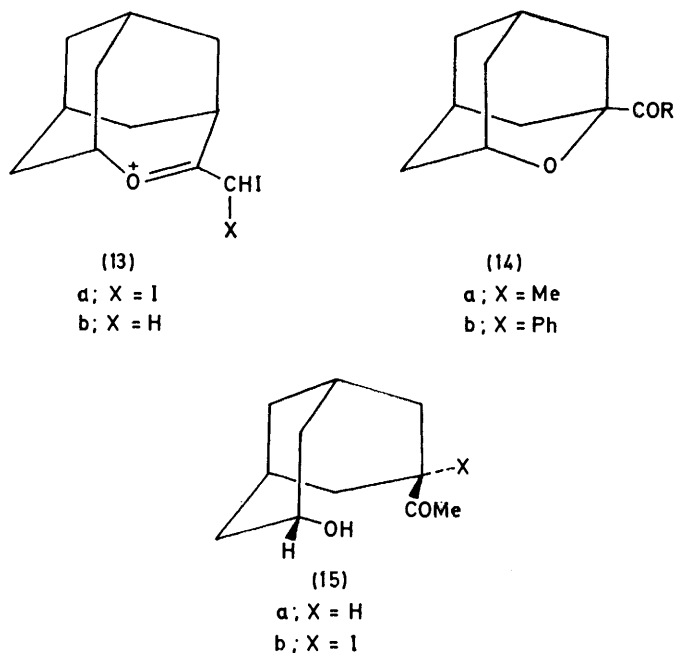
It seems likely that the primary reaction products from (1a–c) are (6a–c), otherwise the reaction of (1c) would fail if the initial oxidative attack on the alcohols and their subsequent rearrangement required direct involvement of the exocyclic carbon atom attached to C(2). The phenyl substituent in (6c) blocks further reactions, whereas in the case of (6b) elimination of HI could occur to give (9b). Electrophilic iodination of (9b) followed by proton loss could then result in the formation of (5a), the product isolated from the reaction. The methyl group in (5a) blocks further reaction, but in the hypoiodite reaction of (1a), the product at this stage would be (9c). Electrophilic iodination of (9c) and subsequent proton loss, as above, would afford (5b), the actual product isolated from the reaction.

It is not at all clear why the iodo-ethers (6) should be formed in place of the radical cleavage products, the iodo-ketones (3), particularly since  $\text{Pb}(\text{OAc})_4\text{-I}_2$  oxidation of adamantan-1-ol proceeds by the 'normal' pathway.<sup>2</sup> Conversely, although hypochlorite thermolyses for the present alcohols (1) proceed normally, the hypochlorite procedure is extremely inefficient for adamantan-1-ol.<sup>2</sup> Assuming that the hypochlorite oxidations *do* involve free radicals (an interpretation that is consistent with the vast majority of the published data on hypochlorite decompositions<sup>8</sup>) it follows that the hypoiodite reactions, at least for the adamantanols, are either non-radical processes or are radical processes but with the close involvement of an iodine or a lead atom. These points were tested by three model experiments. Thermolysis of 2-methyladamantan-2-ol hypochlorite in the presence of iodine gave a complex mixture of iodinated products containing no di-iodo-ether (5b) and whose i.r. spectrum showed only weak carbonyl absorption indicating the virtual absence of (3a) as well. Repetition of the reaction in the presence of both iodine and lead tetra-acetate gave (5b) in 27% yield; (5b) was also obtained in low yield (17%) in the photolytic reaction of (1a) with mercuric oxide and iodine. Reaction of (1a) with iodine in boiling benzene affords only 2-methyleneadamantane. The accumulated results infer that the metal atom has an important mechanistic role besides providing a convenient means for generating electrophilic iodine and thereby allowing the conversion  $\text{ROH} \rightarrow \text{ROI} \rightarrow \text{RO}^\cdot$ . Judging from the rearrangement processes described herein, adamantanol oxidation by  $\text{Pb}(\text{OAc})_4\text{-I}_2$  may have more cationic than free radical character, in contrast to the hypochlorite reactions.

As a working hypothesis, we view the attachment of the adamantoxyl species to an iodine substituted lead

atom. Decomposition of this species with intramolecular delivery of iodine to the alkoxy carbon atom would involve rearrangement (adamantan-2-ols), whereas delivery of iodine to the  $\beta$ -carbon atom would involve fragmentation (adamantan-1-ol). Certainly, the mechanism of alcohol oxidation appears to be more complex than is generally assumed.<sup>8b,9</sup>

*Reactions of the Iodo-olefin (5b) with Hydrochloric Acid.*—Reference has already been made to the conversion of (5b) into the chloromethyl lactol (7d) by the action of hydrochloric acid in chloroform. The mechanism probably involves the sequence of reactions  $(5b) + \text{H}^+ \xrightarrow{\text{Cl}^-} (13a) \xrightarrow{\text{Cl}^-} \text{ICl} + (9c) \xrightarrow{\text{H}^+} (13b) \xrightarrow{\text{H}_2\text{O}} \text{H}^+ + (7c) \xrightarrow{\text{Cl}^-} \text{I}^- + (7d)$ ;  $\text{ICl} + \text{I}^- \rightarrow \text{I}_2 + \text{Cl}^-$ , and the modest yield of (7d) presumably is a reflection of the opportunity



at each stage of diversion to other products. The mechanism is consistent with the observations that reaction with trifluoroacetic and other acids HA with poorly nucleophilic anions  $\text{A}^-$  were inefficient in promoting iodine formation, and that anhydrous LiCl or NaCl were quite ineffective in causing decomposition of (5b).

The major product (60%) isolated from the reaction of (5b) with dilute hydrochloric acid in hot dimethylformamide (DMF) was a liquid ketone identified as methyl 2-oxa-1-adamantyl ketone (14a); small quantities of the chloromethyl lactol (7d) were also isolated. Considerable evolution of iodine had occurred within 10 min and the volatile products (g.l.c.) comprised (14a), (7a), (7d), and an unidentified compound. Variation of the product composition with time (see Experimental section) indicates that (7a) is the kinetically significant intermediate in the change  $(5b) \rightarrow (14a)$ , whereas the lactol (7d) is only a by-product on account of the relatively low concentration of  $\text{Cl}^-$ . Separate reaction of

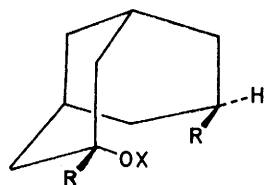
(7d) with dilute HCl-DMF gave (14a) in very low (*ca.* 7%) yield; however, the co-addition of either iodine or sodium iodide promoted the formation of (14a). The immediate but slow evolution of iodine from the sodium iodide reaction suggests  $I_2$  rather than  $I^-$  to be the essential co-reactant; g.l.c. analysis again indicated the intermediacy of (7a). In the parallel reactions of (7a) itself with dilute HCl-DMF only small quantities of (14a) were detected in 6 h even in the presence of sodium iodide. The formation of (14a) was rapidly promoted by the addition of iodine, and to such an extent that it was the only product detected by g.l.c. after 6 h. The results prove the essential intermediacy of both (7a) and  $I_2$ . The suggested reaction mechanism, namely

$$(5b) \xrightarrow{I_2} (13b) \xrightarrow{Cl^-} ICl + (9a) \xrightleftharpoons{H^+ - H_2O} (7a) \xrightleftharpoons{H^+} (15a) \xrightleftharpoons{I_2 - H^+} (15b) \longrightarrow (14a)$$

involves only chemical steps for which there are adequate precedents. The partial conversion of (13b) into (7c) and thence into (7d), as above, explains the isolation of the chloromethyl lactol; the transformation of (7d) into (9a) is presumably a fairly slow reaction.

Reaction of the phenyl-substituted lactol (7b) with dilute HCl-DMF and iodine (1 equiv.) gave the phenyl ketone (14b) (55%). These reactions provide a novel 'one-pot' synthesis of 1-substituted 2-oxa-adamantanes, and the ring contraction strategy could perhaps be applied to other systems. Yields were not optimised, and a complicating factor in the efficient preparation of (14b) was the low solubility of (7b) in aqueous DMF.

*Reaction of (5b) with Methylmagnesium Iodide.*—At the time when (X) was thought to have structure (4) rather than the correct formulation (5b), reaction with an excess of methylmagnesium iodide was studied in order to determine if the C(5) iodine atom could be alkylatively



(16)

- a; R = C≡CMe, X = H  
 b; R = C≡CCD<sub>3</sub>, X = H  
 c; R = CH<sub>2</sub>CH<sub>2</sub>Me, X = H  
 d; R = CH<sub>2</sub>CH<sub>2</sub>CD<sub>3</sub>, X = H  
 e; R = C≡Cl, X = MgI

substituted. An unstable hygroscopic crystalline compound of molecular formula  $C_{12}H_{18}O$  was isolated. Spectroscopic data indicated a secondary alcohol, and probably an *endo*-3-hydroxybicyclo[3.3.1]nonane ( $\tau$  5.99, quintet). The n.m.r. signal due to the added methyl group was located by repeating the experiment using  $CD_3MgI$  giving the position at  $\tau$  8.26 (3 H, d,  $J$  2.4 Hz). Catalytic hydrogenation of the  $C_{12}H_{18}O$  compound resulted in the rapid uptake of 2 mol of hydrogen; the

reduction product was identified as *endo*-7-propylbicyclo[3.3.1]nonan-*endo*-3-ol (16c). Similarly, hydrogenation of the trideuteriomethyl derivative gave (16d). It follows from this and the spectroscopic evidence that the original products were the acetylenic alcohols (16a) and (16b) respectively.

The mechanism envisaged for the transformation of (5b) into (16a) involves preliminary complexation of the MeMgI by the oxygen atom of (5b) followed by a cyclical rearrangement of electrons leading to MeI and the fragmentation product (16e). Alkylation of (16e) by MeMgI and hydrolysis (work-up) would be expected to yield (16a). An interesting partial analogy is to be found in the cleavage of isobutyl vinyl ether by the more reactive reagent phenyl-lithium to give acetylene, lithium isobutoxide, and benzene.<sup>10</sup>

#### EXPERIMENTAL

Instrumentation, conditions, and techniques are as noted previously<sup>11</sup> except that g.l.c. refers to analysis at 150 °C on a 5 ft column packed with polyethyleneglycol adipate on Diatomite C (10% w/w). Light petroleum refers to the fraction with b.p. 60–80 °C and <sup>1</sup>H n.m.r. spectra were recorded for solutions in deuteriochloroform unless stated otherwise. In the i.r. spectral data s = strong, m = medium, w = weak, br = broad.

*2-Methyladamantan-2-ol* (1a) and *2-Ethyladamantan-2-ol* (1b).—These compounds were prepared from adamantan-2-one.<sup>12</sup>

*2-Phenyladamantan-2-ol* (1c).—Adamantan-2-one (7.5 g, 0.05 mol) in dry ether (100 ml) was added to a stirred solution of phenylmagnesium bromide [from magnesium (2.4 g, 0.1 mol) and bromobenzene (15.7 g, 0.1 mol) in ether (75 ml)] at 0 °C. After completion of the addition the mixture was stirred at room temperature for 12 h. Conventional work-up<sup>12</sup> afforded a yellow oil which, after two crystallisations from light petroleum, afforded the *product*<sup>3</sup> (8.11 g, 71%), m.p. 80.5–81 °C (Kofler) (Found: C, 84.2; H, 8.5.  $C_{16}H_{20}O$  requires C, 84.2; H, 8.8%),  $\nu_{max}$  3 620m—w, 1 040m, and 1 005m  $cm^{-1}$ ,  $\tau$  2.35–2.85 (5 H, m, ArH), 7.5br (2 H, s, H-1 and -3), 7.68br (1 H, s), 8.28br (11 H, m, skeletal H), and 8.45 (1 H, s, exchanges with D<sub>2</sub>O, OH).

*2-Trideuteriomethyladamantan-2-ol* (1d).—Reaction of adamantan-2-one (3.0 g, 0.02 mol) in ether (40 ml) with trideuteriomethylmagnesium iodide [from trideuteriomethyl iodide (5.8 g, 0.04 mol) and magnesium (0.92 g, 0.04 mol) in ether (30 ml)] as above afforded colourless needles of the *product* from light petroleum, m.p. 218–220 °C (sealed capillary), in high yield (3.23 g, 96%);  $\nu_{max}$  3 630m—w and 2 220m—w  $cm^{-1}$ ,  $\tau$  7.77 (1 H, m), 7.89 (2 H, m, H-1 and -3), 8.0–8.4 (11 H, complex m, skeletal H), and 8.3 (1 H, s, exchanges with D<sub>2</sub>O, OH).

<sup>13</sup>C-Labelled *2-Methyladamantan-2-ol* (1e).—Methyl iodide containing *ca.* 10 atom % <sup>13</sup>C was prepared by mixing 92 atom % material (1.1 g) with redistilled reagent grade material (1.1 atom %; 10.02 g). The Grignard reagent was prepared from this methyl iodide (11.12 g) and magnesium (1.86 g) in dry ether (65 ml total). Reaction with adamantan-2-one (10.00 g, 0.033 mol) in ether (300 ml) in the usual way and work-up as above afforded colourless needles from light petroleum, m.p. 219 °C (10 g).

*5-Di-iodomethylene-4-oxatricyclo[4.3.1.1<sup>3,8</sup>]undecane* (5b).—(a) A mixture of 2-methyladamantan-2-ol (1.66 g, 0.01

mol), lead tetra-acetate (4.88 g, 0.011 mol), iodine (2.54 g, 0.01 mol), anhydrous calcium carbonate (2 g), and dry benzene (30 ml) was boiled under reflux under nitrogen with vigorous stirring for 1.5 h. The cooled mixture was filtered, the residue washed with ether (100 ml), and the filtrate plus washings extracted successively with 10% w/v sodium thiosulphate-water (50 ml), 5% w/v sodium hydrogencarbonate-water ( $3 \times 25$  ml), and water (25 ml), and dried ( $\text{Na}_2\text{CO}_3\text{-CaCO}_3$ ). Removal of the solvent *in vacuo* at 20 °C gave a yellow solid (2.92 g) which was crystallised twice from light petroleum to give the *di-iodo-ether* (1.4 g), m.p. 149–150 °C (Kofler; slight decomp.) (Found: C, 31.8; H, 3.5; I, 60.4%;  $M^+$ , 415.9126;  $M^+ + 2$ , 417.9211.  $\text{C}_{11}\text{H}_{14}\text{I}_2\text{O}$  requires C, 31.8; H, 3.4; I, 61.0%;  $M^+$ , 415.9137;  $M^+ + 2$ , 417.9201),  $\nu_{\text{max}}$  2927 ( $\epsilon$  313), 2851 (101), 1582 (78, C=C stretch), 1262, 1185 (450), 1108, 1035 (271.5), 582, 530, and 455  $\text{cm}^{-1}$ ;  $\lambda_{\text{max}}$  ( $\text{CHCl}_3$ ) 37370inf. ( $\epsilon$  2200) and 28670 (177)  $\text{cm}^{-1}$ ;  $\lambda_{\text{max}}$  (EtOH) 43960 ( $\epsilon$  11200)  $\text{cm}^{-1}$ ,  $\tau$  (220 MHz) 5.37 (1 H, m, outer line separation 12.5 Hz, H-3), 6.15 (1 H, m, outer line separation 15.2 Hz, H-6), and 7.94–8.41 (12 H, complex m, skeletal H); *m/e* 417 (1%), 416 (8.6), 294 (2), 289 (0.8), 254 (2), 162 (2), 161 (0.7), 134 (1.4), 133 (1.8), 126 (1.6), 121 (0.9), 119 (1), 117 (1), 91 (6.3), 79 (7.2), 67 (4.2), 44 (12.8), and 40 (100);  $d^{17}$  2.26. Further crystallisation of the mother-liquors yielded 2-methyladamantan-2-ol (0.68 g).

The highest yield of the di-iodo-ether (2.16 g, 52%) was obtained using 0.02 mol of the oxidants and crystallisation of the product first from methanol and then from light petroleum. The material is stable for long periods of time only when pure and if stored at or below 0 °C.

Reaction of 2-trideuteriomethyladamantan-2-ol as above afforded a yellow crystalline product identical in all respects to the di-iodo-ether (see also Discussion).

(b) Isotopically labelled (5b) containing *ca.* 10 atom %  $^{13}\text{C}$  at the exocyclic carbon atom was prepared as in (a) from (1e) but using two mol. equiv. of lead tetra-acetate and of iodine, followed by recrystallisation of the product from methanol and then light petroleum. The labelled *iodo-olefin* had m.p. 150 °C;  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ; p.p.m. downfield from  $\text{Me}_4\text{Si}$ ) 165.08 (s, C-5), 75.32 (d, C-3), 36.37 (2 t, C-2 and -11), 36.02 (d, C-6), 34.39 (t, C-9), 33.62 (2t, C-7 and -10), 25.91 (2d, C-1 and -8), and –10.35 (s,  $\text{Cl}_2$ ). The high field signal was intensified by *ca.* ten times over that for the spectrum of natural abundance (5b); this signal split to a doublet ( $J$  3.91 Hz) in the undecoupled spectrum, indicating three-bond allylic coupling with H-6. The superimposed signals at 36.37, 33.62, and 25.91 p.p.m. remained unresolved in spectra recorded for  $\text{C}_6\text{D}_6$  and  $\text{CDCl}_3\text{-C}_5\text{H}_5\text{N}$  (trace) solutions, confirming the plane of symmetry present in the molecule.

(c) A vigorously stirred mixture of (1a) (1.66 g, 0.01 mol), red mercuric oxide (4.34 g, 0.02 mol), iodine (5.58 g, 0.022 mol), and carbon tetrachloride (60 ml) was boiled under reflux under nitrogen with irradiation from a Philips 300 W 'Ultraphil' lamp. After 1.5 h the mixture was cooled and worked up as above to give a yellow oil ( $\nu_{\text{max}}$  3600 w, 1730m, 1718m, and 1582w—m  $\text{cm}^{-1}$ ). Crystallisation from methanol at –10 °C, then light petroleum, gave the di-iodo-ether (5b) (0.69 g, 17%), m.p. 148–150 °C (Kofler). G.l.c. analysis of the mother-liquors indicated unchanged (1a) as the major component of a complex product mixture.

*Reactions of 2-Methyladamantan-2-yl Hypochlorite.*—(a) A solution of the hypochlorite [from (1a) (1.66 g, 0.01 mol) and

chlorine monoxide (0.012 mol);  $\nu_{\text{max}}$  3600  $\text{cm}^{-1}$  absent] in carbon tetrachloride (50 ml) was treated with lead tetra-acetate (4.88 g, 0.011 mol), iodine (2.9 g, 0.011 mol), and benzene (50 ml), and the mixture boiled under reflux with stirring for 3 h. The product was isolated as in the preparation of the di-iodo-ether (5b) to give yellow crystals of the di-iodo-ether (5b) (1.11 g, 27%), m.p. 147–150 °C (Kofler). Further crystallisation of the mother-liquors gave impure 2-methyladamantan-2-ol (0.14 g).

(b) Repetition of experiment (a) but in the absence of lead tetra-acetate and benzene and followed by a similar work-up afforded a solution in  $\text{CCl}_4$  of a complex mixture of products (t.l.c. and g.l.c.) which exhibited  $\nu_{\text{max}}$  3600w, 1740w, 1710w—m, 1700w—m, and 1665w  $\text{cm}^{-1}$ ,  $\tau$  5.6w (s), 5.7w (br), and 7.2–8.8 (m). The only compounds positively identified were (1a) and 2-methyleneadamantane (g.l.c.).

*5-(1-Iodoethylidene)-4-oxatricyclo[4.3.1.1<sup>3,8</sup>]undecane* (5a).—Reaction of 2-ethyladamantan-2-ol (1.8 g, 0.01 mol), lead tetra-acetate (4.88 g, 0.011 mol), iodine (2.54 g, 0.01 mol), anhydrous calcium carbonate (2 g), and dry benzene (30 ml) as above afforded a yellow oil after work-up and showed  $\nu_{\text{max}}$  3650m—w, 1720m—w, 1660m—w, and 1635m—w  $\text{cm}^{-1}$ ;  $\tau$  5.2w (s), 5.5br, 6.4br, 6.6br, 7.6 (s), 8.0–8.6 (m), and 9.13 (t, starting material). The strong singlet at  $\tau$  7.6 was still present when the hydrogencarbonate extraction was omitted from the work-up procedure.

Removal of the solvent from the first fractions obtained from chromatography of the crude reaction product on alumina [eluant light petroleum (b.p. 40–60 °C)–ether 3 : 1 v/v] yielded a white solid (1.02 g, 33%) which crystallised from light petroleum to give colourless needles of the *product* which decomposed on heating above 60 °C or on standing at room temperature (Found: C, 47.7; H, 5.8; I, 42.1.  $\text{C}_{12}\text{H}_{17}\text{IO}$  requires C, 47.4; H, 5.6; I, 41.7%),  $\nu_{\text{max}}$  1635m sh, 1640 (shoulder), 1260m, 1188s, and 1122m  $\text{cm}^{-1}$ ;  $\tau$  5.5 (1 H, m, H-3), 6.6 (1 H, m, H-6), 7.6 (3 H, s, Me), 7.63w (s), and 7.78–8.6 (12 H, m, skeletal H); *m/e* 304 ( $M^+$ , 100%), 182 (21), 177 (75), and 149 (41). Further elution of the chromatography column yielded unchanged 2-ethyladamantan-2-ol (1b) (0.92 g).

*5-Phenyl-4-oxatricyclo[4.3.1.1<sup>3,8</sup>]undecan-5-ol* (7b).—Reaction, as above (2 h), of 2-phenyladamantan-2-ol (1.71 g, 0.0075 mol), lead tetra-acetate (3.66 g, 0.00825 mol), iodine (1.91 g, 0.0075 mol), anhydrous calcium carbonate (1 g), and benzene (25 ml), followed by the usual work-up, gave a brownish solid. A solution of this residue in ether-light petroleum (1 : 1 v/v) was boiled with a little charcoal and filtered. Crystallisation was allowed to commence slowly affording colourless needles of the *product* (0.711 g, 39%) which melted or decomposed over a wide range above 150 °C (Found: C, 78.4; H, 8.3.  $\text{C}_{16}\text{H}_{20}\text{O}_2$  requires C, 78.65; H, 8.25%),  $\nu_{\text{max}}$  3620w—m, 3400br, and 1060s  $\text{cm}^{-1}$ ,  $\tau$  ( $^2\text{H}_6$ )DMSO) 2.5 (2 H, m, ArH), 2.78 (3 H, m, ArH), 4.14 (1 H, s, OH), 5.74 (1 H, m, H-3), 6.42 (1 H, m, H-6), and 7.7–8.7 (12 H, m, skeletal H); *m/e* 244 ( $M^+$ ; 2%), 227 (3), 226 (3), 167 (4), 122 (78), and 80 (100).

*5-Iodomethylene-4-oxatricyclo[4.3.1.1<sup>3,8</sup>]undecane* (9c).—(a) Potassium t-butoxide (1.2 g) was added to a stirred solution of (5b) (1.8 g) in dry dimethyl sulphoxide (18 ml) at 40–45 °C. The mixture was stirred overnight (12 h), poured into water (100 ml), and extracted with light petroleum (b.p. 40–60 °C) ( $5 \times 30$  ml). The extracts were washed with 1% w/v sodium thiosulphate-water (25 ml), water ( $3 \times 30$  ml), and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of the solvent *in vacuo* at room temperature and crystallis-

ation of the residue from light petroleum gave the *iodovinyl ether* as colourless needles (0.977 g, 78%) which decomposed on heating above 70 °C (Found: C, 45.8; H, 5.4; I, 43.0.  $C_{11}H_{15}IO$  requires C, 45.5; H, 5.2; I, 43.8%),  $\nu_{\max}$  3100m—w, 1 612s (sharp), 1 278s, 1 177s, 1 140s, and 1 042s  $cm^{-1}$ ;  $\tau$  ( $CCl_4$ ) 5.32 (1 H, s, =CH), 5.48 (1 H, m, outer line separation *ca.* 14 Hz, H-3), 7.0 (1 H, m, outer line separation *ca.* 18 Hz, H-6), and 7.9—8.5 (12 H, m, skeletal H); *m/e* 290 ( $M^+$ ; 100%), 164 (14), and 163 (23).

Ozonolysis of (9c), under various conditions (including the work-up) afforded the lactone (10) in <10% yield (g.l.c.).

(b) Lithium aluminium hydride (1.50 g) was added to a stirred solution of (5b) (3.0 g) in dry ether (120 ml), and the mixture was stirred at room temperature for 4 h, poured into ice, and filtered. The ethereal layer and ether extracts (2 × 25 ml) of the aqueous phase were combined, washed with water, and dried ( $Na_2SO_4$ ). Removal of the solvent *in vacuo* at 20 °C and crystallisation of the residue from methanol at -78 °C afforded a white solid (1.35 g, 65%) which, after crystallisation from light petroleum had spectroscopic properties identical with the iodovinyl ether (9c) prepared as in (a).

**5-Methylene-4-oxatricyclo[4.3.1.1<sup>3,8</sup>]undecane Dimer (11).**—A mixture of (5b) (3.20 g), zinc dust (1.2 g), glacial acetic acid (1.3 ml), and ether (150 ml) was boiled under reflux with stirring for 18 h, cooled, and filtered. The filtrate was extracted with water (50 ml), 5% w/v sodium hydrogen-carbonate-water (3 × 50 ml), water (50 ml), and dried ( $Na_2SO_4$ ). Removal of the solvent and crystallisation of the residue from aqueous methanol yielded colourless crystals of the *dimer* (1.17 g; 93%), m.p. 139—141 °C (Kofler) (Found: C, 80.5; H, 9.5%;  $M^+$ , 328.236 8.  $C_{22}H_{32}O_2$  requires C, 80.5; H, 9.8%;  $M$ , 328.240 2),  $\nu_{\max}$  1 649m (sharp), 1 250s, 1 155m, 1 120s, and 1 045s  $cm^{-1}$ ;  $\tau$  ( $CCl_4$ ) 5.46 (1 H, s, =CH), 5.73 (1 H, m), 6.0 (1 H, m), 7.3—8.6 (26 H, m), and 8.70 (3 H, s, Me); *m/e* 328 (5%), 314 (30), 313 (100), 207 (7), 191 (20), 189 (9), and 164 (13).

**5-Methyl-4-oxatricyclo[4.3.1.1<sup>3,8</sup>]undecan-5-ol (7a).**—(a) The iodovinyl ether (9c) (0.580 g, 0.002 mol) and platinum oxide (0.020 g) in ethanol (30 ml) were shaken with hydrogen at atmospheric pressure. After 12 h *ca.* 45 ml (*ca.* 0.002 mol) of hydrogen had been absorbed; the solution was filtered, poured into water (100 ml), and extracted with ether (3 × 25 ml). The extracts were washed with 1% w/v sodium thiosulphate-water (20 ml) and water, and dried ( $Na_2SO_4$ ). Removal of the solvent and crystallisation of the residue from light petroleum afforded the *lactol* (0.190 g, 52%) which decomposed on heating above 100 °C (Found: C, 72.4; H, 9.7.  $C_{11}H_{16}O_2$  requires C, 72.5; H, 9.95%),  $\nu_{\max}$  3 630w—m, 3 400br, 1 142m, 1 112s, 1 064m, 1 034m, and 928m  $cm^{-1}$ ;  $\tau$  ( $CCl_4$ ) 5.87 (1 H, m, H-3), 7.0 (1 H, s, exchanges with  $D_2O$ , OH), 7.4—8.45 (13 H, m, skeletal H), and 8.48 (3 H, s, suffers intensity reduction with  $D_2O$ , Me); *m/e* 167 (12%), 166 (8), 165 (8), 164 (10), and 80 (100) ( $M^+$  absent).

Repetition of the reaction in the presence of potassium hydroxide (0.25 g) resulted in the uptake of *ca.* 45 ml of hydrogen in 4 h. Isolation of the product afforded material identical with that above (0.237 g; 65%).

(b) Lithium aluminium hydride (0.3 g) was added to a stirred solution of tri-*n*-butyltin chloride (1.5 g) in ether (20 ml).<sup>13</sup> After 10 min the di-iodo-ether (5b) (1.5 g) in ether (50 ml) was added and the mixture boiled under reflux for 16 h. The cooled mixture was poured onto ice

and extracted with ether, and the extracts were washed with water and dried ( $Na_2SO_4$ ). The lactol was isolated and purified as above (0.141 g, 22%). The mother-liquor from the crystallisation contained a complex mixture of products (t.l.c., alumina-benzene) and was not investigated further.

**endo-2-(3-endo-Hydroxybicyclo[3.3.1]nonan-7-yl)propan-2-ol (8a).**—(a) The lactol (7a) (0.250 g) in ether (25 ml) was added to a stirred solution of methylmagnesium iodide [from methyl iodide (1.42 g) and magnesium (0.24 g)] in ether (25 ml). The mixture was boiled under reflux for 14 h and poured into concentrated aqueous ammonium chloride (10 ml). The ethereal layer and ether extracts (2 × 25 ml) of the aqueous phase were washed with water and dried ( $Na_2SO_4$ ), the solvent removed, and the residue crystallised from light petroleum to give the *diol* (0.211 g, 78%), m.p. 133—134 °C (Kofler) (Found: C, 27.7; H, 11.0.  $C_{12}H_{22}O_2$  requires C, 27.7; H, 11.2%),  $\nu_{\max}$  3 400s (br), 1 142m, and 1 092m  $cm^{-1}$ ;  $\tau$  5.88 (1 H, m, outer line separation *ca.* 16 Hz, H-3), 7.15 (2 H, s, exchange with  $D_2O$ , 2 × OH), 7.6—8.5 (13 H, m, skeletal H), and 8.86 (6 H, s, Me).

(b) Reaction of the lactone (10) (0.800 g)<sup>11</sup> in dry ether (50 ml) with a stirred solution of methylmagnesium iodide [from methyl iodide (7.1 g) and magnesium (1.2 g)] in ether (50 ml) was allowed to proceed for 12 h and then worked-up as in (a) to give a white residue (0.820 g). Slow crystallisation from light petroleum gave the diol (8a, 0.311 g), m.p. 133—134 °C (Kofler), identical with the material prepared in (a). Chromatography of the mother-liquors on neutral alumina (eluant chloroform-light petroleum 1 : 1) gave the lactol (7a) (0.165 g) in the first fractions. Further elution of the column yielded an impure ketone (formed by degradation on the column) of unknown constitution.

**endo-1-(3-endo Hydroxybicyclo[3.3.1]nonan-7-yl)-1-phenylethanol (8b).**—A solution of the lactol (7b) (0.250 g) in ether (80 ml) was added to a stirred solution of methylmagnesium iodide [from methyl iodide (1.42 g) and magnesium (0.24 g)] in ether (25 ml). The mixture was boiled under reflux for 14 h, and subsequently worked-up as in the preceding preparation (a) to give the *product* as colourless needles (0.188 g; 71%), m.p. 127—130 °C (Kofler) (Found: C, 78.5; H, 9.1.  $C_{17}H_{24}O_2$  requires C, 78.4; H, 9.3%),  $\nu_{\max}$  3 390s (br), 1 125m, and 1 065m  $cm^{-1}$ ;  $\tau$  2.4—2.9 (5 H, m, ArH), 5.89 (1 H, m, outer line separation *ca.* 15 Hz, H-3), 6.4 (2 H, s, exchange with  $D_2O$ , 2 × OH), 7.7—9.0 (13 H, m, skeletal H), and 8.56 (3 H, s, Me).

**5-Iodomethyl-4-oxatricyclo[4.3.1.1<sup>3,8</sup>]undecan-5-ol (7c).**—Elution of the iodovinyl ether (9c) (0.20 g) over silica with chloroform followed by removal of the solvent and crystallisation of the residue from light petroleum afforded the *iodomethyl lactol* as colourless needles (0.154 g; 72%) which decomposed on heating above 70 °C (Found: C, 43.05; H, 5.5; I, 41.7.  $C_{11}H_{17}IO_2$  requires C, 42.75; H, 5.5; I, 41.2%),  $\nu_{\max}$  3 590w—m, 3 400br, 1 139m, and 1 044s  $cm^{-1}$ ;  $\tau$  ( $CCl_4$ ) 5.82 (1 H, m, H-3), 6.38 (1 H, d, *J* 10 Hz,  $CH_2I$ ), 6.64 (1 J, d, *J* 10 Hz,  $CH_2I$ ), 7.28 (1 H, s, exchanges with  $D_2O$ , OH), and 7.35—8.6 (13 H, m, skeletal H); *m/e* 290 (23%), and 167 (100) ( $M^+$  absent).

**5-Chloromethyl-4-oxatricyclo[4.3.1.1<sup>3,8</sup>]undecan-5-ol (7d).**—Concentrated hydrochloric acid (1 ml) was added dropwise to a rapidly stirred solution of the di-iodo-ether (5b) (1.0 g) in chloroform (10 ml). The evolution of iodine was immediate. The solution was stirred at room temperature for 10 min, diluted with chloroform (20 ml), and extracted with water (20 ml), 10% w/v sodium metabisulphite (20 ml),

7% w/v sodium hydrogencarbonate ( $3 \times 20$  ml), and water (20 ml), and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of the solvent *in vacuo* and crystallisation of the residue twice from light petroleum afforded the *chloromethyl lactol* (0.240 g; 46%), m.p. 127–128 °C (Kofler) (Found: C, 60.9; H, 7.9.  $\text{C}_{11}\text{H}_{17}\text{ClO}_2$  requires C, 60.95; H, 7.9%),  $\nu_{\text{max}}$  3 600m—w, 3 400br, 1 150m, 1 132m, 1 060s  $\text{cm}^{-1}$ ;  $\tau$  5.77 (1 H, m, H-3), 6.33 (2 H, s,  $\text{CH}_2\text{Cl}$ ), 7.16 (1 H, s, exchanges with  $\text{D}_2\text{O}$ , OH), and 7.45 (13 H, m, skeletal H);  $\tau$  ( $[\text{}^2\text{H}_6\text{O}]\text{DMSO}$ ) 4.36 (1 H, s, OH), 5.95 (1 H, m, H-3), 6.24 (1 H, d,  $J$  11 Hz,  $\text{CH}_2\text{Cl}$ ), 6.52 (1 H, d,  $J$  11 Hz,  $\text{CH}_2\text{Cl}$ ), and 7.5–8.6 (13 H, m, skeletal H);  $m/e$  216, 200 (4%), 198 (12), 180 (7), 167 (67), 163 (35), and 80 (100) ( $M^+$  absent).

Removal of the solvent from the mother-liquors yielded an unstable solid comprising a mixture (t.l.c.) containing vinyl ethers ( $\nu_{\text{max}}$  1 610–1 645  $\text{cm}^{-1}$ ).

Various control reactions of (5b) were also conducted (see Discussion).

*Methyl 2-Oxa-1-adamantyl Ketone* (14a).—(a) A mixture of the di-iodo-ether (5b) (1.0 g), dimethylformamide (DMF) (13 ml), and 0.67M-hydrochloric acid (10 ml) was stirred at 105 °C for 6 h, poured into water (100 ml), and filtered to yield a pale yellow solid (0.014 g) with spectroscopic properties identical to the chloromethyl lactol (7d). The filtrate was extracted with ether ( $3 \times 30$  ml) which was washed with water and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of the solvent and distillation of the residue gave the *ketone* (0.259 g; 60%) as a colourless mobile oil, b.p. 65–70 °C (bath) at 0.01 mmHg (Found: C, 73.9; H, 9.1%;  $M^+$ , 180.116 7.  $\text{C}_{11}\text{H}_{16}\text{O}_2$  requires C, 73.3; H, 8.95%;  $M$ , 180.115 023),  $\nu_{\text{max}}$  1 708s and 1 025m  $\text{cm}^{-1}$ ;  $\tau$  ( $\text{CCl}_4$ ) 5.90 (1 H, m, H-3), 7.82 (2 H, m), 7.94 (3 H, s, Me), and 8.0–8.5 (10 H, m, skeletal H);  $m/e$  180 ( $M^+$ ; 45%), 137 (100), and 43 (26).

(b) The above reaction was repeated (1/10th scale) with monitoring (g.l.c.) of the volatile products. Approximate product ratios were estimated from peak areas and revealed the following changes as a function of time: 10 min (14a) 30%, (7d) 21%, (7a) 46%, unknown product 3%; 70 min (14a) 73%, (7d) 18%, (7a) 6%, unknown product 3%; 130 min (14a) 76%, (7d) 18%, (7a) 6%, unknown product < 1%; 300 min (14a) 85%, (7d) 8%, (7a) 7%, unknown product < 1%.

(c) Treatment of the chloromethyl lactol (7d) (0.054 g, 0.000 25 mol) in DMF (1.2 ml) at 105 °C with 0.67M-hydrochloric acid (1.2 ml) and stirring for 6 h gave a mixture containing (14a) (7%) and unchanged (7d) (50%) (g.l.c.). Repetition of the experiment with added sodium iodide (0.075 g, 0.000 5 mol) resulted in the immediate evolution of iodine. G.l.c. indicated the mixture to contain (14a) (93%) and (7a) (7%) as the only detectable volatile products. In this case, the product composition as a function of time was: 5 min (14a) 16%, (7d) 56%, (7a) 20%, unknown product 8%; 60 min (14a) 30%, (7d) 26%, (7a) 38%, unknown product 6%; 300 min (14a) 82%, (7d) 17%, (7a) 1%, unknown product < 1%.

(d) The first part of experiment (c) was repeated in the presence of added iodine (0.064 g, 0.000 25 mol) to afford (14a) (82%) and (7a) (18%) (g.l.c.).

(e) Reaction of the lactol (7a) (0.046 g, 0.000 25 mol) in DMF (1.2 ml) and 0.67M-hydrochloric acid (1.2 ml) at 105 °C for 6 h gave a complex mixture of products containing (14a) (7%). Repetition of the experiment in the presence of added sodium iodide (0.075 g, 0.000 5 mol) afforded a complex mixture containing (14a) (16%). The use of added iodine (0.064 g, 0.000 25 mol) in place of the

sodium iodide, however, gave a high yield of (14a) as the only detectable volatile product.

*2-Oxa-1-adamantyl Phenyl Ketone* (14b).—The lactol (7b) (0.244 g, 0.001 mol) and iodine (0.254 g, 0.001 mol) were stirred at 105 °C in DMF (15 ml) and 0.67M-hydrochloric acid (5 ml) for 6 h. The mixture was poured into water (50 ml) and the aqueous solution extracted with ether ( $3 \times 25$  ml), and the extracts were washed with water and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of the solvent and slow distillation of the residue afforded the *product* (0.133 g, 55%), b.p. 125–130 °C (bath) at 0.1 mmHg (Found: C, 79.9; H, 7.6%;  $M^+$ , 242.131 9.  $\text{C}_{16}\text{H}_{18}\text{O}_2$  requires C, 79.3; H, 7.5%;  $M$ , 242.130 672),  $\nu_{\text{max}}$  1 678s, 1 602w—m, 1 268m, and 1 021m  $\text{cm}^{-1}$ ;  $\tau$  ( $\text{CCl}_4$ ) 1.88 (2 H, m, ArH), 2.70 (3 H, m, ArH), 5.77 (1 H, m, H-3), and 7.6–8.55 (12 H, m, skeletal H);  $m/e$  242 ( $M^+$ , 60%), 137 (100), 105 (91), and 77 (32).

*endo-7-(Prop-1-ynyl)bicyclo[3.3.1]nonan-3-endo-ol* (16a).—A solution of the di-iodo-ether (5b) (2.09 g, 0.005 mol) in dry ether (125 ml) was added to a stirred solution of methylmagnesium iodide [from methyl iodide (14.2 g, 0.1 mol) and magnesium (2.3 g, 0.1 mol)] in ether (50 ml); stirring was continued, at room temperature, for 14 h. The mixture was poured into concentrated aqueous ammonium chloride (25 ml), and the ethereal layer and ether extracts ( $2 \times 30$  ml) of the aqueous phase were washed with 1% w/v sodium thiosulphate–water (20 ml) and water ( $2 \times 50$  ml), and dried ( $\text{Na}_2\text{SO}_4$ ). Removal of the solvent *in vacuo* and crystallisation of the residue from light petroleum at –10 °C afforded colourless needles of the *alkynol* (0.53 g, 60%), m.p. 71.5–73 °C (Kofler) (Found: C, 81.2; H, 10.2.  $\text{C}_{12}\text{H}_{18}\text{O}$  requires C, 80.9; H, 10.2%),  $\nu_{\text{max}}$  3 660w—m, 3 500br, 1 120m, and 1 054m  $\text{cm}^{-1}$ ;  $\tau$  ( $\text{CCl}_4$ ) 5.99 (1 H, quint., outer line separation 22 Hz, H-3), 7.45br (1 H, m, H-7),<sup>14</sup> 7.7–8.2 (10 H, m), 8.26 (3 H, d,  $J$  2.4 Hz, Me),<sup>14</sup> 8.59 (2 H, m, approximates to d, separation 4.5 Hz), and 8.67 (1 H, s, exchanges with  $\text{D}_2\text{O}$ , OH);  $m/e$  178 ( $M^+$ , 30%) and 91 (100). It was necessary to store this material *in vacuo* at 0 °C to avoid its decomposition.

*endo-7-(Trideuterioprop-1-ynyl)bicyclo[3.3.1]nonan-3-endo-ol* (16b).—Reaction of the di-iodo-ether (5b) with trideuteriomethylmagnesium iodide as in the preparation of (16a) above (2/5th scale), afforded the *labelled alkynol* as white needles (0.171 g, 47%), m.p. 69–72 °C;  $\tau$  ( $\text{CCl}_4$ ) 6.0 (1 H, quint., outer line separation 22 Hz, H-3), 7.46 (1 H, quint., outer line separation 22.5 Hz, H-7), 7.7–8.3 (10 H, m), 8.62 (2 H, m approximates to d, separation 9 Hz), and 9.0 (1 H, s, exchanges with  $\text{D}_2\text{O}$ , OH);  $m/e$  181 ( $M^+$ , 100%). This material required storage as for (16a).

*endo-7-Propylbicyclo[3.3.1]nonan-3-endo-ol* (16c).—The alkynol (16a) (0.100 g) in methanol (25 ml) was shaken with platinum oxide (10 mg) and hydrogen at atmospheric pressure. The theoretical quantity of hydrogen was absorbed within 2 h whereupon the solution was filtered, the solvent removed *in vacuo*, and the residue crystallised from light petroleum (40–60 °C) at –78 °C to give white *crystals* (0.071 g, 70%), m.p. 83–84 °C (Kofler) (Found: C, 79.2; H, 12.1.  $\text{C}_{12}\text{H}_{22}\text{O}$  requires C, 79.1; H, 12.2%),  $\nu_{\text{max}}$  (KBr) 3 330s (br), 1 120m, and 974s  $\text{cm}^{-1}$ ;  $\tau$  5.88 (1 H, m, outer line separation 19 Hz, CHO), 7.7–9.0 (17 H, m), and 9.16 (3 H, t,  $J$  6.6 Hz, Me);  $m/e$  182 ( $M^+$ , 8%), 180 (10), 164 (100), and 121 (93).

*endo-7-(3,3,3-Trideuteriopropyl)bicyclo[3.3.1]nonan-3-endo-ol* (16d).—The deuteriated alkynol (16b) (0.030 g) in methanol (10 ml) was hydrogenated and the product isolated as for (16c) to give white *crystals* (0.19 g, 60%),



m.p. 80—83 °C (Kofler),  $\tau$  5.89 (1 H, m, outer line separation 19 Hz, CHO), 7.7—9.2 (17 H, m);  $m/e$  185 ( $M^+$ , 6%), 183 (10), 167 (70), 124 (63), 121 (70), and 80 (100).

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