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The Transformation of Cyclic Alcohols into Cyclic Acetals through a New Oxygen Atom Insertion by Photolysis in the Presence of Lead Tetraacetate and Iodine[1)]

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Photolysis of the hypoiodites of steroidal cyclic homoallyl alcohols such as cholesterol and of cyclic alcohols such as 5α-androstan-17β-ol generated in situ in benzene with three molar equivalents each of lead tetraacetate and iodine was found generally to result in the unprecedented formation of corresponding lactol acetates in yields up to 66%. The lactol acetates are readily hydrolysed to lactols in most cases during their isolation and lactols are isolated products. Thus, cholesterol gave 4-oxa-*A*-homocholest-5-en-3-ol and its acetate in a 53% yield. The products differ considerably from those reported by us after the photolysis of the hypoiodites by using mercury(II) oxide and iodine as the reagents for generating the hypoiodites; they also differ from those in the oxidation of the steroidal alcohols with lead tetraacetate alone. The photolysis of the hypoiodite of 2,2-dimethyl-5β-cholestan-3-ol was found to lead to the formation of an anomalous lactol, 2α-iodomethyl-2β-methyl-4-oxa-*A*-homo-5α-cholestan-4ξ-ol together with normal lactol. We discuss the paths of the formation of the lactol acetates involving β-scission of the alkoxyl radicals. A new process was found in the photolysis of 2-indanol hypoiodite in the presence of lead tetraacetate and iodine. Our previously suggested pathways to the formation of 3α,5-epoxy-6-iodo-4-oxa-*A*-homo-5α-cholestanes and 3-formyloxy-2-iodo-2,3-seco-*A*-norcholest-5-ene in the photolysis of cholesterol hypoiodite in the presence of mercury(II) oxide and iodine were supported by the results of the photolysis of 4-oxa-*A*-homocholest-5-en-3-ol hypoiodite in the presence of mercury(II) oxide and iodine.

In our previous papers,[2)] we have reported that the photo-induced reaction of the hypoiodites of steroidal cyclic homoallyl alcohols such as cholesterol (**1**) and several methyl-substituted cholest-5-en-3-ols generated in situ in benzene by an excess of mercury(II) oxide and iodine resulted in several typical products arising from the allyl radical intermediates generated by β-scission of the alkoxyl radicals. Typically, the hypoiodite of cholesterol (**1**) in benzene containing an excess of mercury(II) oxide and iodine underwent photoinduced rearrangement to give 3α,5-epoxy-6β- and 6α-iodo-4-oxa-*A*-homo-5α-cholestanes (**2**) and (**3**) together with 3- formyloxy-2-iodo-2,3-seco-*A*-norcholest-5-ene (**4**).[2a)]

^{18}O Labeling studies using Hg^{18}O disclosed that the products such as **2**, **3**, and **4** are formed via new multi-step processes involving the intra- and intermolecular reactions of intermediary allyl radicals, generated by β-scission of the corresponding alkoxyl radicals, with I_2O, as outlined in Scheme 1.[3)]

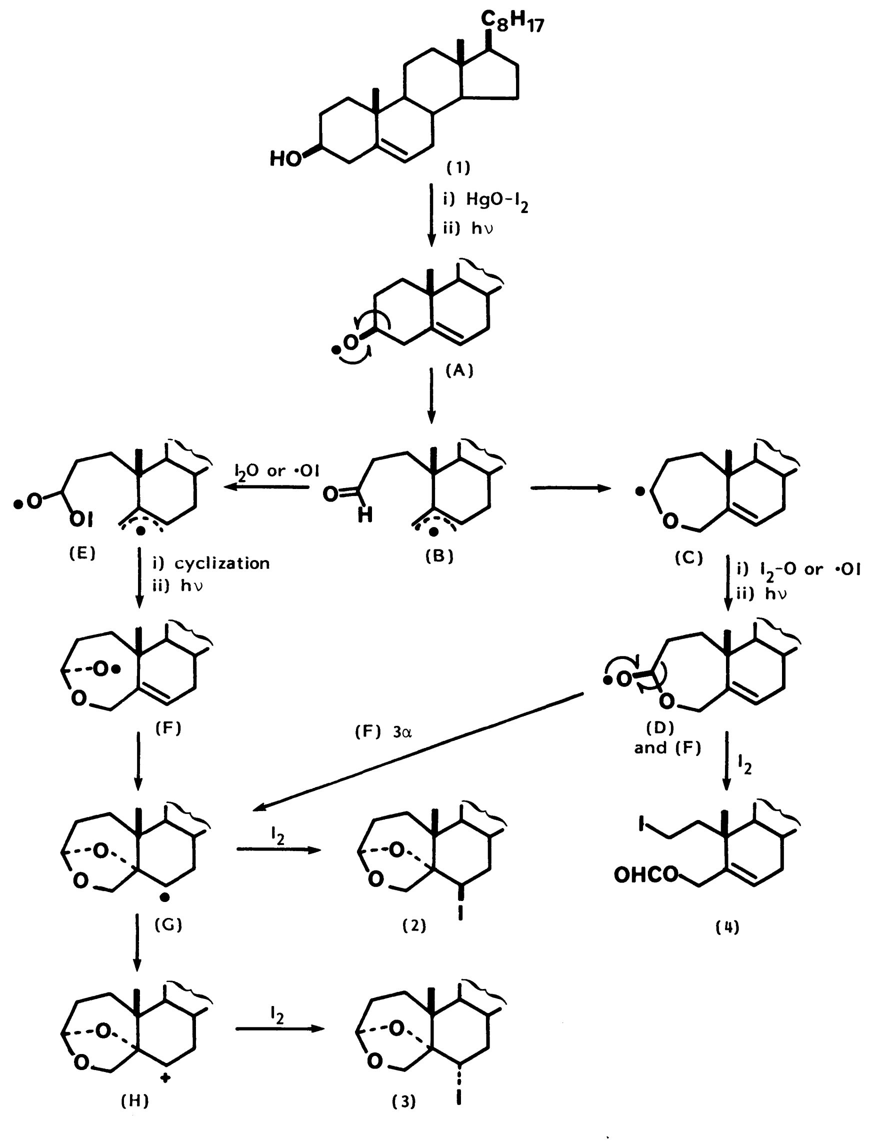
All alkyl hypoiodites used in these photoinduced reaction were prepared by the reaction of cyclic alcohols with iodine oxide (I_2O) generated in situ from mercury(II) oxide and iodine.[4)] Another reagent which has been proved to be useful for generating alkyl hypoiodites from alcohols is a combination of lead tetraacetate and iodine.[5)] This reagent has been extensively used for the intramolecular functionalization of nonactivated carbons, particularly in the steroid field by a Swiss group.[5,6)]

In this paper, we describe the results of photo-induced reactions of the hypoiodites of steroidal cyclic homoallyl alcohols and cyclic alcohols such as cholesterol (**1**) and 5α-androstan-17β-ol (**40**) generated by lead tetraacetate–iodine reagent. The investigation was aimed at comparing a mercury(II) oxide–iodine reagent and a lead tetraacetate–iodine reagent in the photo-induced reactions of the hypoiodites of cyclic alcohols. These comparisons were thought likely to shed further light on the roles of these reagents in the hypoiodite photolysis.

As we describe below, the products of the photoinduced reactions of the hypoiodites generated by lead tetraacetate–iodine are lactol acetates which are formed in fair to good yields by the hydroxyl oxygen insertion and thus differ considerably from those obtained by using mercury(II) oxide–iodine. The reaction is a new version of the reactions which are performed by the lead tetraacetate–iodine reagent.

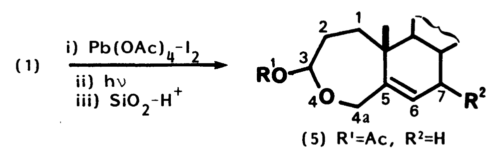
Results

Products of the Photoinduced Reactions of Hypoiodites of Steroidal Cyclic Homoallyl Alcohols. We have chosen cholesterol (**1**) and 4,4-dimethylcholesterol (**19**)[7)] as steroidal cyclic homoallyl alcohols. The photoinduced reaction of cholesterol hypoiodite in benzene in the presence of an excess of lead tetraacetate and iodine has already been reported to give a novel ether, cholest-5-en-3β-yl 4-oxa-*A*-homocholest-5-en-3α-yl ether (**11**) in a 23% yield.[8)] We then went on to investigate the reaction in more detail and found that the products of the reaction hinge on the amounts of the lead tetraacetate and iodine used. Irradiation of cholesterol (**1**) in dry benzene containing 3 mol equiv each of lead tetraacetate and



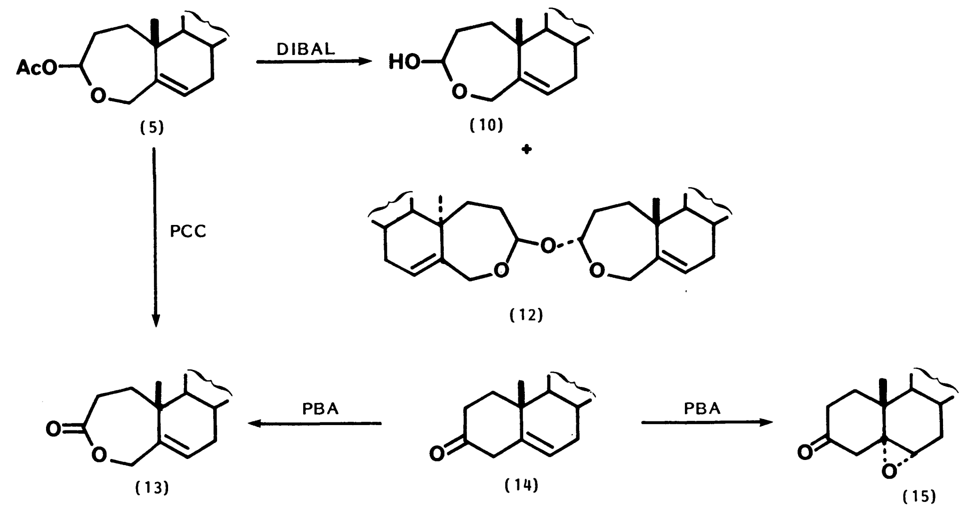
Scheme 1.

iodine in a Pyrex vessel with a light generated by a 100-W high pressure Hg arc lamp for 4.5 h gave a product mixture. Isolation of the products by preparative TLC gave four products [1], [2], [3], and [4] in an order of increasing polarity. The product [1], $C_{29}H_{48}O_3$ (high-resolution mass spectrometry), obtained in a 47% yield showed a band due to an acetoxyl group in the IR spectrum. The ^{1}H NMR spectrum showed a 3H singlet at δ 2.07, a pair of doublets (2H) at δ 3.70 and 4.41 (J=12.5 Hz), a 1H broad doublet at δ 5.64 and a doublet of doublet (1H) (J=6.84 and 4.41 Hz) at δ 6.00. These signals are assigned to the acetoxyl protons, an isolated methylene group having an oxygen atom, an olefin proton, and a proton attached to the carbon atom carrying two oxygen substituents. Its EIMS showed an ion at m/z 384 as the base peak, a peak derived by the elimination of acetic acid from the molecular ion. These spectral results enabled us to assign the structure of the product [1] to 4-oxa-*A*-homocholest-5-en-3ξ-ol acetate (**5**) (Scheme 2). This structure was subsequently confirmed by transforming it into the compounds recorded in the literature. Thus, the reduction of acetate **5** with DIBAL (diisobutylaluminium hydride) in toluene afforded two compounds **10** and **12**. The major and more polar product **10** (56%) was identified



(5) R¹=Ac, R²=H
(6) R¹=Ac, R²=α-OAc
(7) R¹=Ac, R²=β-OAc
(8) R¹=H, R²=α-OAc
(9) R¹=H, R²=β-OAc
(10) R¹=R²=H
(11) R¹=cholest-5-en-3β-yl, R²=H

Scheme 2.



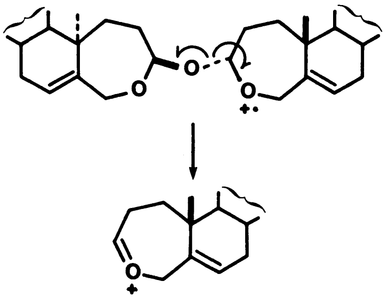
DIBAL: diisobutylaluminium hydride
PBA: perbenzoic acid
PCC: pyridinium chlorochromate

Scheme 3.

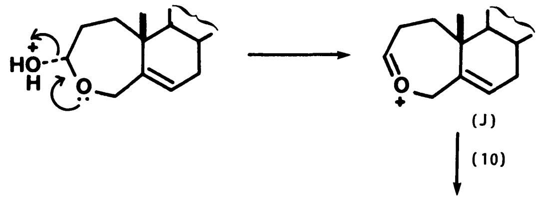
as a mixture of 4-oxa-*A*-homocholest-5-en-3α- and 3β-ol,† a product of the acidic hydrolysis[2a] of cholest-5-en-3β-yl 4-oxa-*A*-homocholest-5-en-3α-yl ether (**11**) previously obtained in this photolysis[8] and in the thermolysis of cholesterol hypoiodite in the presence of mercury(II) oxide and iodine in benzene.[2a]

The less polar minor product **12** (8%) proved to be a dimeric acetal. FIMS (field ionization mass spectrometry) showed that the molecular ion at *m/z* 786 corresponded to the molecular formula $C_{54}H_{90}O_3$. The IR spectrum proved the absence of hydroxyl and carbonyl groups. The ^{1}H NMR spectrum was very similar to that of 4-oxa-*A*-homocholest-5-en-3-ol (**10**). These spectral results strongly suggested that product **12** is a dimer of lactol **10**. The assigned structure is also consistent with the spectrum of the EIMS (electron impact mass spectrometry) which showed the base peak at *m/z* 385, attributable to an ion (I) in Scheme 4. A probable genesis of this dimeric acetal involving the reaction of an intermediary oxonium ion (*J*)[9] with lactol **10** is outlined in Scheme 5.

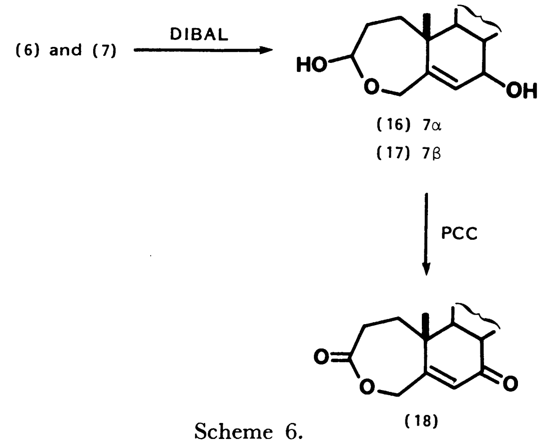
Oxidation of acetate **5** with PCC (pyridinium chlorochromate) gave 4-oxa-*A*-homocholest-5-en-3-one (**13**) which has been obtained together with an epoxide **15** by the oxidation of cholest-5-en-3-one (**14**) with perbenzoic acid[10] (Scheme 3).



Scheme 4.



Scheme 5.



Scheme 6.

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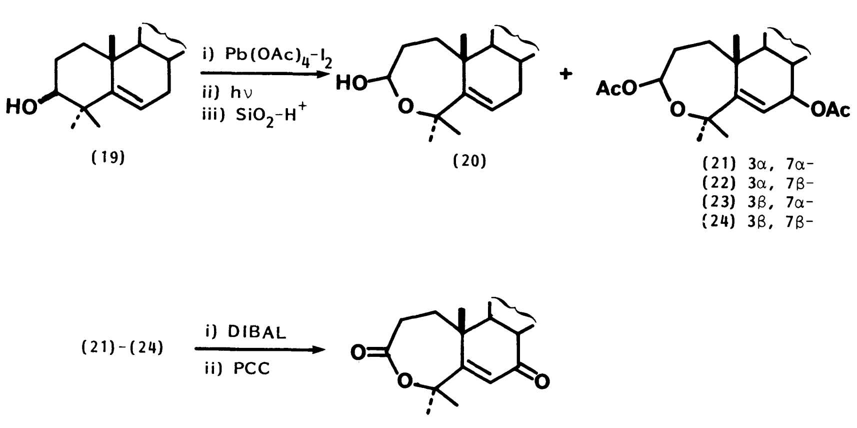
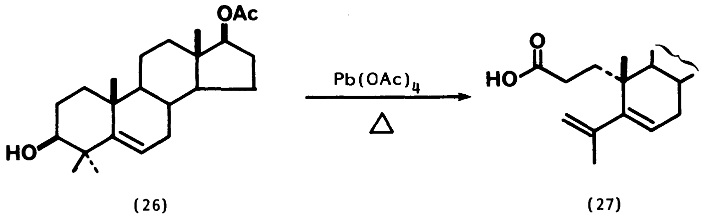
† 4-Oxa-*A*-homocholest-5-en-3α-ol reported in the previous paper[2a] may also be a mixture of 3α- and 3β-isomers. Its ^{1}H NMR spectrum (270 MHz) (see Experimental) proved that the chemical shifts of the 3-H, 4a-H, 5-H, and 18-H of 3α- and 3β-isomers are nearly identical but the 19-H of 3α-isomer differs from that of 3β-isomer. The spectrum also proved the presence of a trace of the corresponding ring-opened aldehyde. It is very likely that in solution the 3α- and 3β-isomers and the ring-opened aldehyde are in an equilibrium.



Scheme 7.



Scheme 8.

The ^{1}H NMR spectrum of the product [2], $C_{31}H_{51}O_5$ (high-resolution mass spectrometry) indicates that it is a stereoisomeric mixture of 4-oxa-*A*-homocholest-5-en-3ξ,7α- (**6**) and 3ξ,7β-diol diacetate (**7**); the IR spectrum indicated a band at 1728 cm^{-1} (OAc). The details of the analysis of the signals in the ^{1}H NMR spectrum of product [2] are recorded in the experimental section. The ratio of diacetates **6** and **7** was found to be 4:1 on the basis of the ratio of the area of the signals due to 7β-H and 7α-H of diacetates **6** and **7**. Their structures were confirmed by further transformations of the mixture. Reduction of the mixture with DIBAL gave a 3:1 mixture of 7α- **16** and 7β-hydroxylactol **17** which was then oxidized with PCC to give a crystalline 4-oxa-*A*-homocholest-5-en-3,7-dione **18** (Scheme 6). The spectroscopic results of dione **18** was fully consistent with the assigned structure (see Experimental).

The product [3] (7% yield) was 4-oxa-*A*-homocholest-5-en-3ξ,7α-diol 7-acetate (**8**) contaminated with its 7β-isomer **9** and their ring-opened aldehydes. The results of the analysis of the ^{1}H NMR spectrum is described in the experimental section.

The product [4] (6%) was identical with the 4-oxa-*A*-homocholest-5-en-3-ols (**10**) obtained by the reduction of lactol acetate **5** with DIBAL. Not a trace of cholest-5-en-3β-yl 4-oxa-*A*-homocholest-5-en-3α-yl ether (**11**), which was reported to be the product in this photoinduced reaction,[8] was found in the products in this experiment.

We then found that cholest-5-en-3β-yl ether **11** is formed at the expense of lactols **5**—**10** if a smaller amount of lead tetraacetate and iodine is used in this reaction. Thus the photolysis of cholesterol hypoiodite prepared by 2 mol equiv of lead tetraacetate and iodine instead of 3 mol. equiv gave cholestenyl ether **11**[2a,8),††] in a 13% yield together with 4-oxa-*A*-homocholest-5-en-3ξ-ol acetate (**5**) (12%), a stereoisomeric mixture of 4-oxa-*A*-homocholest-5-en-3ξ,7β- (**6**) and 3ξ,7β-diol diacetate (**7**) (8%), 4-oxa-*A*-homocholest-5-en-3-ols (**10**)[2a] (11%), and a recovered cholesterol (13%).

A photoinduced reaction of 4,4-dimethylcholest-5-en-3β-ol hypoiodite prepared in situ by the treatment of the 3β-ol **19**,[7] with 3 mol equiv each of lead tetraacetate and iodine was then studied in order to examine the generality of the new reaction found for cholesterol hypoiodite. The irradiation of the hypoiodite in benzene under the conditions as described for the photoreaction of cholesterol gave a mixture of products which were separated by preparative TLC to give products [5] and [6]. The less polar product [5] (4%) was found to be 4a,4a-dimethyl-

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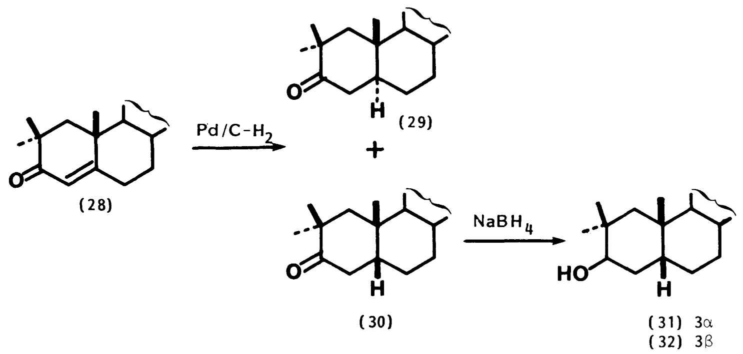
[††] The formation of cholestenyl ether **11** by using 3 mol equiv each of lead tetraacetate and iodine has been reported in the previous paper.[8] An explanation for this is that while a commercial lead tetraacetate was used in the present experiment, a freshly prepared lead tetraacetate used in the previous experiment was contaminated by some acetic acid.



Scheme 9.

4-oxa-*A*-homocholest-5-en-3ξ-ol (**20**) on the basis of the analysis of the ^1H NMR which is described in the experimental section. The more polar product [6] was found to be a mixture of the four possible stereoisomers of 4a,4a-dimethyl-4-oxa-*A*-homocholest-5-en-3,7-diol diacetate **21—24** by the analysis of the ^1H NMR spectrum (see Experimental) (Scheme 7). The assigned structure was further ascertained by transforming it into a crystalline 4a,4a-dimethyl-4-oxa-*A*-homocholest-5-ene-3,7-dione (**25**) by its reduction with DIBAL to 7-hydroxylactols followed by the oxidation with PCC.

The oxidation of 4,4-dimethylandrost-5-ene-3β,17β-diol 17-acetate (**26**) with lead tetraacetate alone has been reported by Amorosa et al.,[11] to give a seco aldehyde **27** in a 28% yield, as outlined in Scheme 8. The different results obtained by the two reagents may thus be apparent.

Products of the Photoinduced Reactions of the Hypoiodites of Steroidal Cyclic Alcohols and 2-Indanol. As was expected, the irradiation of cyclic alcohol hypoiodites under the foregoing conditions similarly gives lactol acetates in better yields in one step if the alkoxyl radicals generated from the hypoiodites are susceptible to β-scission.

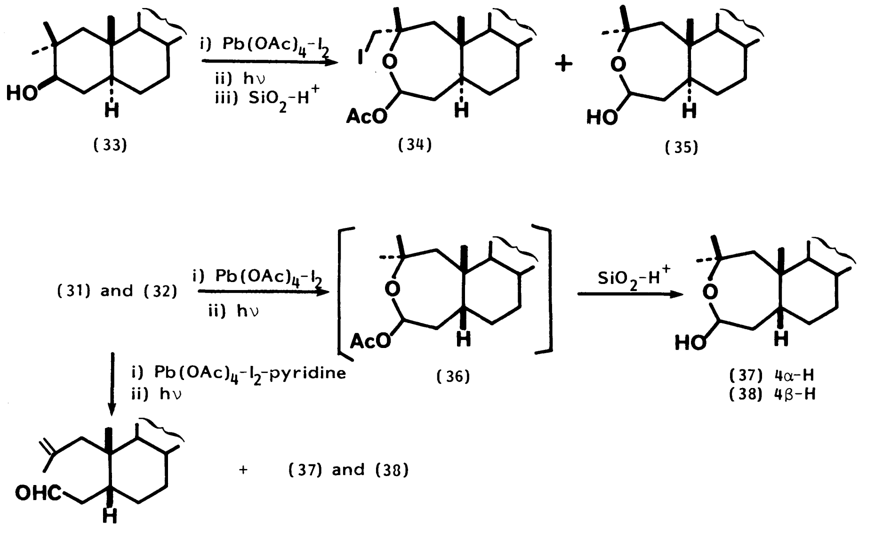
We describe the results with steroidal alcohols, i.e. 2,2-dimethyl-5β-cholestan-3α- (**31**) and 3β-ol (**32**), 2,2-dimethyl-5α-cholestan-3β-ol (**33**),[12] 5α-androstan-17β-ol (**40**),[12] and 2-indanol (**45**) below. A mixture of 3-alcohols **31** and **32**, and 3β-alcohol **33** were prepared by reduction of the corresponding ketones with $NaBH_4$ (Scheme 9). Thus, 2,2-dimethylcholest-4-en-3-one (**28**)[13] was hydrogenated in the presence of palladium-charcoal as a catalyst to afford 2,2-dimethyl-5α-cholestan-3-one (**29**) identical with the authentic specimen and its isomer, 2,2-dmethyl-5β-cholestan-3-one (**30**) in a 3:17 ratio. The structure of the latter was apparent from its spectroscopic data (see Experimental). Reduction of 5β-isomer **30** with $NaBH_4$ gave approximately a 1:1 mixture of 2,2-dimethyl-5β-cholestan-3α-ol (**31**) and 3β-ol **32** (Scheme 9). The separatioh of the isomeric alcohols by means of preparative TLC was unsuccessful.

The preparation of the hypoiodite of 3β-alcohol **33** by the reaction with 3 mol equiv each of lead tetraacetate and iodine and irradiation of the solution under the conditions above gave two products **34** and **35**. The molecular formula of the less polar product **34**, which carries an iodine atom, was established to be $C_{28}H_{49}OI$ by an exact mass measurement of the ion due to $(M-CH_3COOH)^+$. The IR spectrum indicated the presence of an acetoxyl group. The ^1H NMR spectrum proved that the one of the *gem*-dimethyl of the starting 3β-ol was lost and exhibited only one 3H singlet at δ 1.44 attributable to Me group beside the two singlets due to the 18- and 19-H. It also showed a 3H singlet attributable to an acetoxyl group, and a 2H broad singlet at δ 3.40 assignable to a methylene group having an iodine. Thus, the structure of product **34** should be 2α-iodomethyl-2β-methyl-4-oxa-*A*-homo-5α-cholestan-4ξ-ol which can accommodate all the foregoing spectral results. The iodomethyl group attached to the C-2 of this lactol acetate **34** should be α-oriented since the chemical shift of the signal due to the 19-H (δ 1.03) does not differ appreciably from that of the signal due to the 19-H (δ 1.02) of product **35** for which the structure, 2,2-dimethyl-3-oxa-*A*-homo-5α-cholestan-4ξ-ol, was deduced on the basis of the mass spectrum together with the spectroscopic data (see Experimental).

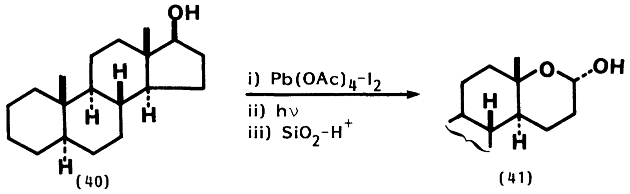
Similar irradiation of the hypoiodites of 3α- and 3β-ols **31** and **32** in benzene under the conditions as for 3β-ol **33** and the separation of the product by means of preparative TLC gave a 1:1 mixture of 2,2-dimethyl-3-oxa-5β-cholestan-4α-(**37**) and 4β-ols (**38**) in a 66% yield. The structures were deduced by means of the IR, ^1H NMR and mass spectra (see Experimental). When this photolysis was carried out by adding a small amount of pyridne, an appreciable amount of a seco-aldehyde **39** (27%) was formed as an accompanying product at the expense of the yields of the lactols.

The irradiation of the hypoiodite of 5α-androstan-17β-ol (**40**),[12] a typical steroidal five-membered cyclic alcohol, in benzene under the conditions as described above, gave 17a-oxa-D-homo-5α-androstan-17α-ol (**41**) in a 24% yield. The product **41** was identical with the specimen prepared by Baeyer–Villiger oxidation of 5α-androstan-17-one followed by its reduction with DIBAL.[15] The difference in the product **41** with those reported for the oxidation of steroidal 17β-ol **42** with lead tetraacetate alone by Amorosa et al,[11] which is outlined in Scheme 12, is again apparent.

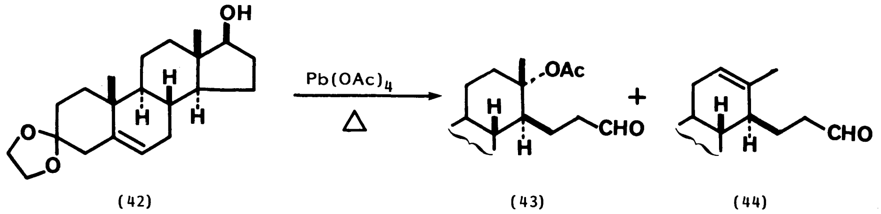
Finally, we undertook the photolysis of 2-indanol hypoiodite which should generate a stabilized benzyl radical by a β-scission of the corresponding alkoxyl radicals. We found that the major product was 2,3-dihydro-1*H*-2-benzopyran-3-ol acetate (**46**) (23% yield),



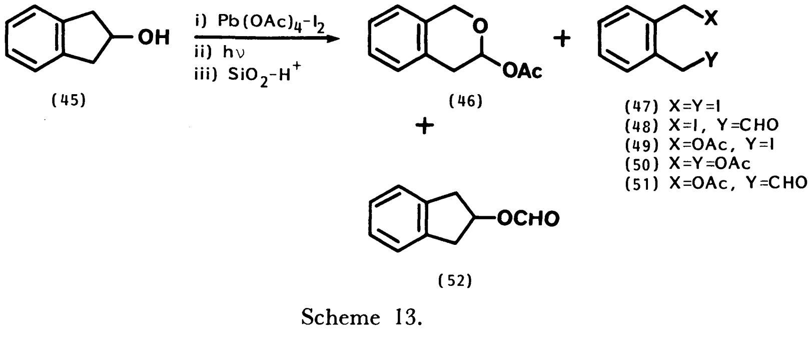
Scheme 10.



Scheme 11.



Scheme 12.

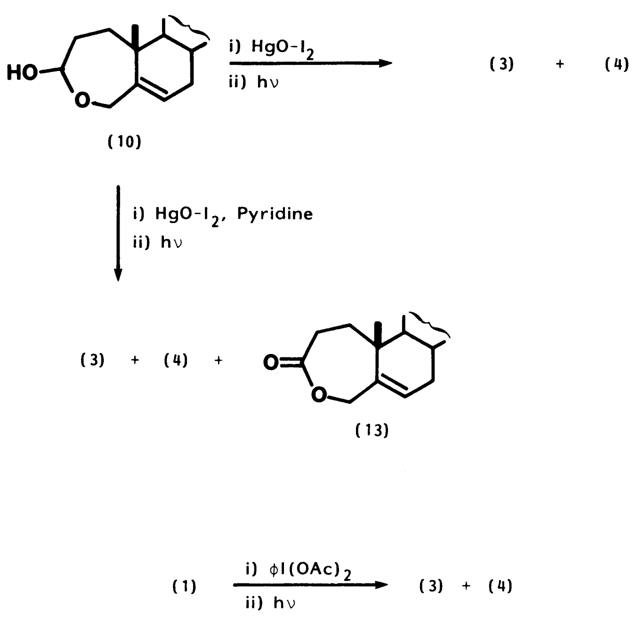


Scheme 13.

while several minor products **47**—**51**, arising from the combinations between the benzyl radical or cation and ·OAc, ⁻OAc, or iodine, as well as 2-indanol formate (**52**), were obtained in low yields (Scheme 13).

Products of the Photoinduced reaction of the Hypoiodite of 4-Oxa-A-homocholest-5-en-3-ols (10) in the Presence of Mercury(II) Oxide and Iodine. As we mentioned at the outset of this paper, the photolysis of hypoiodite of cholesterol (**1**) in benzene containing an excess of mercury(II) oxide and iodine gives 3α,5-epoxy-6β- and 6α-iodo-4-oxa-*A*-homo-5α-cholestanes (**2**) and (**3**) together with iodo formate **4**.[2a,3] It has recently been reported that (diacetoxyiodo) benzene is a good reagent for the production of hypoiodite from alcohols.[16] We therefore prepared cholesterol hypoiodite from (diacetoxyiodo)benzene and cholesterol and subjected it to photolysis. It was found that 3α,5-epoxy-6α-iodo-4-oxa-*A*-homo-5α-cholestane (**3**) and iodo formate **4** are the major products and that no 6β-iodooxasteroid **2** was found in the product. The difference in the products when mercury(II) oxide–iodine and (diacetoxyiodo)benzene are used to generate hypoiodites is interesting.

As outlined in Scheme 1, the paths leading to these products should involve the intermediacy of alkoxyl radicals such as (D) or (F). These species can be generated by the irradiation of the hypoiodites of 3α- and 3β-lactols **10**. In order to ascertain the proposed paths outlined in Scheme 1, the products of the photolysis of the hypoiodites of lactols **10** were studied. Irradiation of lactols **10** in benzene containing 3 mol equiv each of mercury(II) oxide and iodine was found to give oxasteroid **3** (17%) and iodo formate **4** (56%), as otulined in Scheme 14. This photolysis was also carried out in the presence of pyridine. We found that besides oxasteroid **3** (11%) and iodo formate **4** (39%), lactone **13**[10] is formed in a 25% yield. The results can be taken as a further evidence that the immediate forerunners of 3α,5-epoxy-4-oxa-*A*-homosteroids such as **3** and iodo formate **4** in the steroid-5-en-3-ol hypoiodite photolysis are alkoxyl radicals (D) and (F). Pyridine accelerates the formation of lactone **13**. No further experiments have been carried out to clear up the problem as to why radical (G) is more readily oxidized to give cation (H), from which 6α-iodo compound **3** is believed to be formed, in the case of the photolysis of lactol hypoiodite.



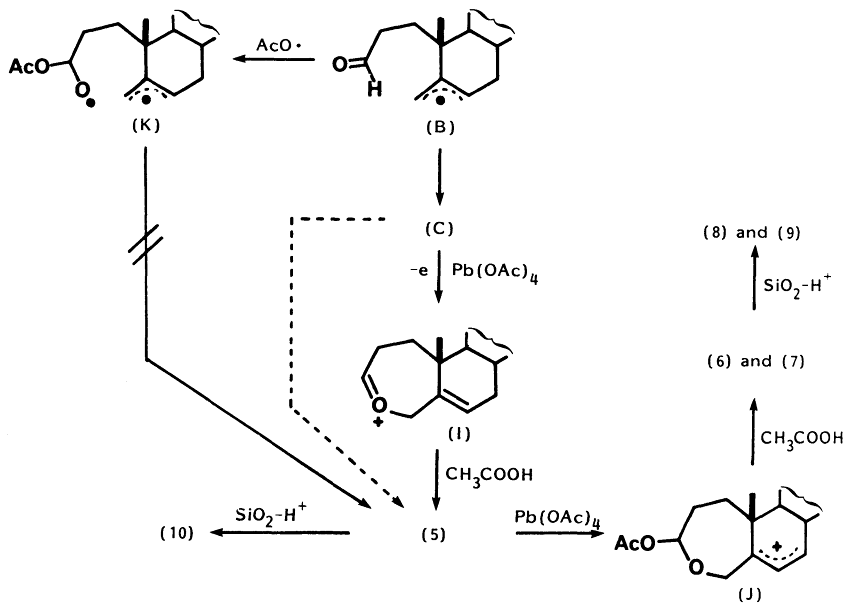
Scheme 14.

Discussion

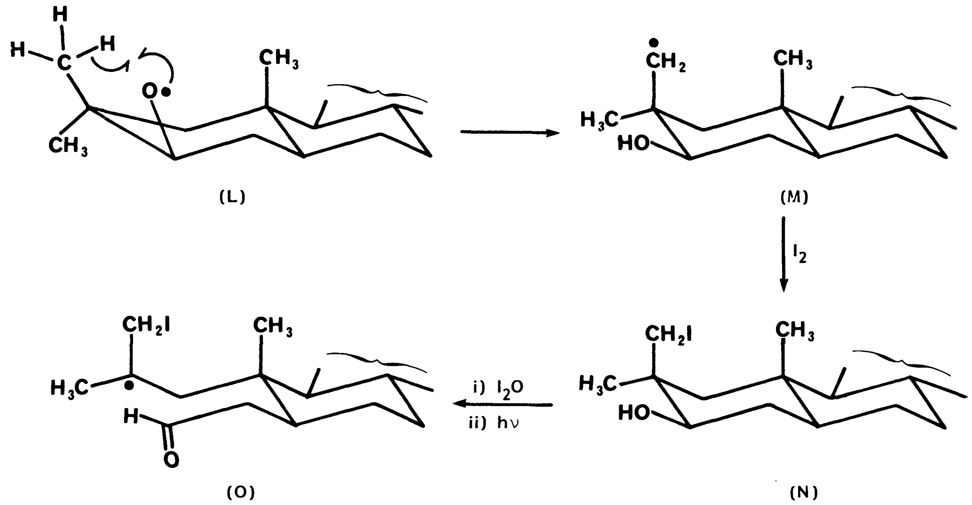
The foregoing experiments clearly show that the products in the photolysis of the hypoiodites of cyclic alcohols generated in situ in benzene with three molar equivalents each of lead tetraacetate and iodine differ considerably from those in a photolysis using mercury(II) oxide and iodine[2] as the reagent for generating the hypoiodites; the photolysis generally results in the formation of the lactols or their acetates by an oxygen insertion and no 3α,5-epoxy-4-oxa-*A*-homo-5α-cholestanes such as **2** and **3** and iodo formate **4**[2a,3] are formed. The formation of the lactols from the cyclic alcohols in one step is unprecedented.

We confirmed that no reaction took place when the above cyclic alcohols in benzene containing lead tetraacetate alone were irradiated and an intractable mixture resulted when cholesterol in benzene containing lead tetraacetate was heated under reflux.

The probable paths for the formation of the lactols and their acetates in the present study are outlined in Scheme 15. The cyclic alcohols are transformed into the corresponding hypoiodites with CH_3COOI generated in situ by the reaction of lead tetraacetate with iodine.[5,6] The excited hypoiodites generate the corresponding alkoxyl radicals which rearrange to the allyl radicals (B) by β-scission. Its intramolecular combination with the carbonyl oxygen then generates the radicals (C). Thus, the formation of lactol acetates may well follow the same path as that in the photoinduced reaction by using mercury(II) oxide and iodine up to the formation of the intermediate (C). The one-electron oxidation of the radical (C) with lead tetraacetate generates an oxonium ion (I) which traps acetic acid to give lactol acetates (**5**). An alternative formation of lactol **5**, although less likely, by a radical combination between radical (C) and an acetoxyl radical may also be possible. The formation of **5** via a biradical (K) is very unlikely since a β-scission may precede from species (K). The parent cyclic alcohols such as cholesterol can apparently compete with acetic acid in the reaction with the oxonium ion (I) to form an ether such as **11**[8] when a concentration of the lead tetraacetate-iodine reagent is lower. Lactol



Scheme 15.

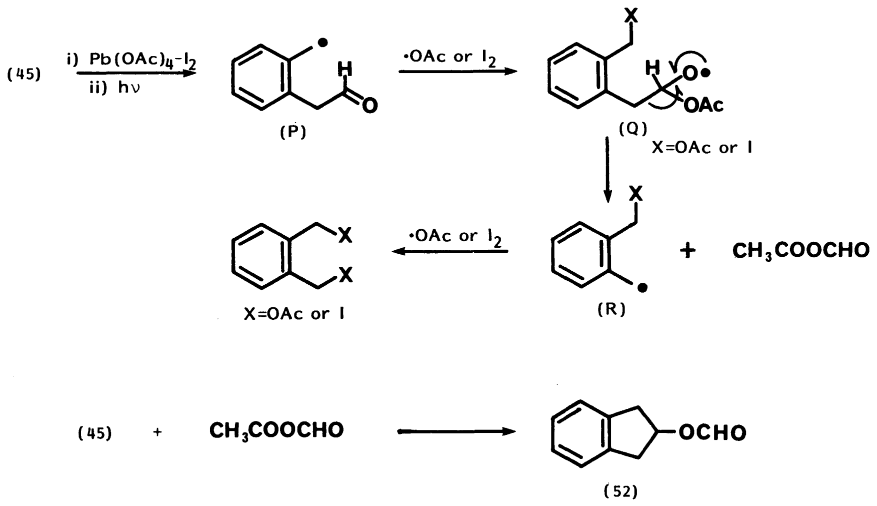


Scheme 16.

acetates **6** and **7** are formed by oxidation of acetates **5** with lead tetraacetate or through a hydrogen abstraction of the allylic hydrogen with acetoxyl radical to form an allyl radical followed by its oxidation to an allyl cation which traps acetic acid. The formation of the lactols alone or with the corresponding acetates have been observed for all the photolysis of the present hypoiodite photolysis. It is clear that these lactols are not the primary products but that they are formed by hydrolysis with silica gel in preparative TLC. The formation of these lactols by preparative TLC of the lactol acetates was in fact confirmed for some of the lactol acetates. It is interesting to note that no lactols corresponding to the lactol acetates **21**—**24** and **34** were found after the treatment with silica gel (preparative TLC), nor were lactol acetates corresponding to lactols **5**, **35**, **37**, **38**, and **41** isolated in preparative TLC with silica gel. These different patterns of behavior of the initially formed lactol acetates are apparently ascribable to hindrance by nearby substituents.

The formation of anomalous lactol acetate **34** which carries an iodine atom (Scheme 10) is interesting. Scheme 16 outlines its formation from the alkoxyl radical (L). The ring A should adopt a somewhat flattened chair conformation owing to the 1,3-diaxial interaction between 2*β*- and 10*β*-Me groups. The alkoxyl radical (L), therefore, can abstract a hydrogen of the 2*β*-Me via a normally incapable five-membered transition state to form a carbon-centred radical (M) which then abstracts an iodine atom to give a new intermediate (N). The path from the intermediate (N) to the lactol acetate **34** via (O) is straightforward.

Finally, all the products with the exception of formate **52** formed in the photolysis of 2-indanol hypoiodite should be derived by a radical (P) arising



Scheme 17.

from a β-scission of 2-indanyloxy radical as outlined in Scheme 17. The simultaneous formation of formate **52** and products **47**, **49**, and **50** strongly suggests the involvement of an intermediate (Q) which can be generated by the attack of an acetoxyl radical on a formyl group of an intermediary aldehyde. The β-scission of the alkoxyl radical (Q) may give acetic formic anhydride and a new benzyl radical (R). The former then reacts with 2-indanol to give formate **52**[17] while the reaction of the latter with iodine or an acetoxyl radical leads to products **47**, **49**, and **50**.

The present photoinduced reaction can be useful in synthesis since the lactols can be obtained in yields as high as 66% in one step from cyclic alcohols provided the alkoxyl radicals generated from them are susceptible to β-scission. Even the unsaturated lactols such as **5** and **20** which are not easily obtainable by other methods can be obtained in one step from cyclic homoallyl alcohols.

Experimental

Mps were determined with a Yanagimoto micro mp apparatus. IR spectra were determined for Nujol mulls by a Hitachi Model 285 infrared spectrometer unless stated otherwise. ^{1}H NMR spectra was determined by a Hitachi-R-90H spectrometer (90 MHz) or JEOL-JMS-GX-270 spectrometer (270 MHz) (solvent $CDCl_3$: $SiMe_4$ as internal standard). Mass spectra were taken by JEOL JMS-D300 spectrometer (70 eV) (Faculty of Pharmaceutical Sciences of this University). TLC was carried out on Merck Kiesel gel 60 PF_{254}. Elemental analyses were performed by the staff of the Faculty of Pharmaceutical Sciences.

Lead Tetraacetate. A quality of lead tetraacetate was found to affect considerably to the yields of each product. Throughout the present work, a commercial lead tetraacetate was used.

The Photolysis of Cholesterol Hypoiodite in the Presence of Lead Tetraacetate and Iodine. (a) Cholesterol (**1**) (1 g, 2.59 mmol) in benzene (120 mg) containing lead tetraacetate (3.44 g, 7.77 mmol) and iodine (1.97 g, 7.74 mmol) was irradiated under an atmosphere of a nitrogen for 4.5 h. TLC indicated that no starting material remained unchanged. After the removal of the precipitates by filtration, the solution was washed with 5% sodium thiosulfate solution, 5% sodium hydrogencarbonate solution, water and saturated brine successively and dried (Na_2SO_4). After the usual work-up the residue (1.464 g) was subjected to preparative TLC with a benzene–diethyl ether (10:1) to give three fractions. The most mobile fraction (551 mg, 47%) was an oily lactol acetate (**5**). ^{1}H NMR (200 MHz) 0.69 (3H, s, 18-H), 0.98 (3H, s, 19-H), 2.07 (3H, s, OAc), 3.70 (1H, d, J=12.5 Hz, 4a-H), 4.41 (1H, d, J=12.5 Hz, 4a-H), 5.64 (1H, br.d, 6-H), and 6.00 (1H, dd, J=6.84 and 4.41 Hz, 3-H); IR (neat) 1733 (OAc), 1222 (C–O), and 1005 (C–O); MS (70 eV) m/z (rel intensity) 444 (M^+, 0.3), 384 ($[M-CH_3COOH]^+$, 100), 328 (39.9), 247 (36.8), and 215 (42.8). Found: $(M-CH_3COOH)^+$ 384. 33626. Calcd for $C_{27}H_{44}O$: $M-CH_3COOH$, 384.33916.

The second mobile fraction (233 mg) was a mixture of lactols **8** and **9** and their acetates **6** and **7**. This was again subjected to preparative TLC with benzene and diethyl ether (2:1)to give two fractions A (181 mg) and B (79 mg, 6.6%). The more mobile fraction A was again subjected to preparative TLC with hexane and diethyl ether (1:1) to give an oily mixture of two epimers of lactol acetate **6** and **7** (49 mg, 3.8%). ^{1}H NMR (200 MHz) 0.68 (3H, s, 18-H of two C-7 epimers), 0.98 (3H, s, 19-H) of C-7 epimers), 2.03 (3H, s, Ac), 2.08 (3H, s, Ac), 3.74 (1H, d, J=13.19 Hz, 4a-H of two epimers), 4.40 (0.2H, d, J=13.19 Hz, 4a-H of 7β-acetoxy epimer), 4.44 (0.8H, d, J=13.19 Hz, 4a-H of 7α-acetoxy epimer), 5.00 (0.8H, br.t, J=4.4 Hz, 7β-H of 7α-acetoxy epimer), 5.12 (0.2H, dd, J=2 and 8.6 Hz, 7α-H of 7β-acetoxy epimer), 5.47 (0.8H, d, J=2 Hz, 6-H of 7β-epimer), 5.77 (0.2H, d, J=4.88 Hz, 6-H of 7α-epimer), 6.01—6.41 (1H, m, 3-H of 7α- and 7β-epimers); MS (70 eV) m/z (rel intensity) 502 (M^+, 0.2), 442 ($[M-CH_3COOH]^+$, 23), 400 (30), and 43 (100); IR (neat) 1728 (OAc), 1243 (C–O), and 1020 (C–O). Found: M^+ 502.36289. Calcd for $C_{31}H_{50}O_5$: M, 502.37569. The less mobile fraction B was a gummy 7α-acetoxylactol **8** contaminated with 7β-acetoxylactol **9** and the corresponding ring-opened aldehydes. ^{1}H NMR (90 MHz) 0.66 (s, 18-H of 7α-acetoxylactol), 0.69 (s, 18-H of 7β-acetoxylactol), 0.94 (s, 19-H of 7α-acetoxylactol), 1.01 (s, 19-H of 7β-acetoxylactol), 2.00 (s, OAc of 7β-acetoxylactol), 2.02 (s, OAc of 7β-acetoxylactol), 3.60 (br.d, J=12 Hz, 4a-H of 7α- and 7β-acetoxylactols), 4.51 (br.d, J=12 Hz, 4a-H of 7α- and 7β-acetoxylactols), 4.06 (br.s, 4a-methylene group of ring-opened aldehyde), 4.95—5.05 (m, 7-H of 7α- and 7β-acetoxylactols and their ring-opened aldehydes), 5.09—5.15 (m, 3-H of 7α- and 7β-acetoxylactols), 5.42 (d, J=2 Hz, 6-H of 7β-acetoxylactol), 5.74 (d, J=5.6 Hz, 6-H of 7α-acetoxylactol), and 9.72 (br.s, CHO of the ring-opened aldehydes); IR 3400 cm^{-1} (OH), 1718 (OAc), 1237 (C–O), and 1020 (C–O); MS (70 eV) m/z (rel intensity) 442 ($[M-H_2O]^+$ of lactols, 3.6%), 400 ($[M-AcOH]^+$ of lactols 47), and 43 (100).

The third fraction (19 mg) was 4-oxa-*A*-homocholest-5-en-3-ol (**10**) which was identical with the authentic specimen.

(b) Cholesterol (100 mg, 0.26 mmol) in benzene (15 ml) containing lead tetraacetate (228 mg, 0.52 mmol) and iodine (131 mg, 0.52 mmol) was irradiated under an atmosphere of a nitrogen for 4 h. TLC of the reaction mixture indicated the presence of some cholesterol. The reaction mixture was worked up as described above. The crude product (153 mg) was subjected to preparative TLC with a benzene–diethyl ether (10:1) to give five fractions a to e. The most mobile fraction a was a mixture and therefore subjected again to preparative TLC with a benzene–hexane (1:1) to give a dimeric acetal **11** (27 mg, 14%) which was identical with the authentic specimen. The next mobile fraction b (14 mg, 12%) was lactol acetate **5**. The fraction c (11 mg, 8%) was a mixture of lactol acetates **6** and **7** judged from the ^{1}H NMR spectrum. Fraction d (13 mg) was cholesterol. Fraction e was lactols **10**.

Reduction of Lactol Acetate 5 with DIBAL. The lactol acetate **5** (81 mg) in dry toluene (8 ml) was cooled by Dry Ice–methanol. To this solution DIBAL (1 M hexane solution, Ventron) (0.22 ml) was added by means of micro syringe. After the solution was stirred for 2 h, water was added and the reaction mixture was stirred for half an hour. After the precipitates were removed by filtration, the organic layer was washed with brine and dried over anhydrous sodium sulfate. Usual work-up of the solution gave a residue which showed two spots on TLC plate. The product was subjected to preparative TLC with benzene–diethyl ether (5:1) to give two products. The more mobile compound (11 mg, 7.6%) was a dimeric acetal **12** which was recrystallized from dichloromethane. Mp 225—231 °C. FDMS (rel intensity) m/z 786 (M^+, 77%), 768 (40), 385 (100, the ion I in the text). ^{1}H NMR (200 MHz) 0.68 (6H, s, 18 and 18'-H), 0.89 (6H, s, 19 and 19′-H), 4.30 (2H, d, J=13.3 Hz, 4a- and 4a′-H), 4.95—5.20 (2H, m, 3 and 3′-H), 5.50—5.62 (2H, m, 6- and 6′-H); IR 1257 and 1020 cm^{-1} (C–O). The less mobile compound (41 mg, 56%) was a mixture of 3α- and 3β-lactols **10**. ^{1}H NMR 0.69 (s, 18-H of 3α- and 3β-isomers), 0.97 (s, 19-H of 3α-isomer), 0.93 (s, 19-H of 3β-isomer), 3.58 (br.d,J=13 Hz, 4a-H of 3α- and 3β-isomers), 4.48 (d, J=13 Hz, 4a-H of 3α- and 3β-isomers), 5.17 (br.t, 3β- and 3α-H of 3α- and 3β-isomers), 5.62 (br.dd, J=2 and 5 Hz; 5-H of 3α- and 3β-isomers), 9.75 (br.t, CHO of the ring opened aldehyde).

Oxidation of Lactol Acetate 5 with Pyridinium Chlorochromate (PCC). To the lactol acetate **5** (41 mg) in dichloromethane (7 ml) containing some Celites, PCC (30 mg) was added and the solution was stirred for 2 h. After the solution was filtered, the filtrate was washed with water and then a brine successively and dried over anhydrous sodium sulfate After the usual work-up, the crude product was purified by means of preparative TLC to give a pure 4-oxa-*A*-homocholest-5-en-3-one (**13**) (30 mg, 70%). Analytical specimen was obtained by recrystallization from methanol. Mp 200—202 °C (lit,[10] 202 °C). ^{1}H NMR (90 MHz) 0.69 (3H, s, 18-H), 1.07 (3H, s, 19-H), 4.20 (1H, d, J=13.2 Hz, 4a-H), 4.78 (1H, d, J=13.2 Hz, 4a-H), and 5.84 (1H, br.dd, J=6.2 and 2.2 Hz); IR 1733 cm^{-1} (lactonic C=O), 1288, 1155, and 1035; MS (70 eV) m/z (rel intensity) 400 (M^+, 51.6), 385 ($[M-15]^+$, 22.1), 287 (82.3), and 43 (100).

Reduction of Lactol Acetates 6 and 7 with DIBAL. The lactol acetates (63 mg) in dry toluene (6 ml) was reduced with DIBAL (0.26 ml) as described for the reduction of lactol acetate **5**. The product (47 mg) was subjected to preparative TLC with diethyl ether to give a 3:1 mixture of gummy lactols **16** and **17** (24 mg, 61%). ^{1}H NMR (90 MHz) 0.69 (3H, s, 18-H), 0.96 (3H, s, 19-H), 3.60 (1H, br.d, J=13 Hz, 4a-H), 4.52 (1H, br.d, J=13 Hz, 4a-H), 3.87 (1H, br.s, 7-H), 5.08—5.23 (1H, m, 3-H), 5.53 [0.24H, br.d, J=2 Hz, 6-H of (**14**)], 5.78 (0.75H, br.d, J=5.3 Hz, 6-H of (**13**)]; IR 3340 cm^{-1} (OH) and 1027 (C–O); MS (70 eV) m/z (rel intensity) 418 (M^+, 6.7), 400 ($[M-H_2O]^+$, 23), 353 (57), and 55 (100). Found: M^+ 418.34219. Calcd for $C_{27}H_{46}O_3$: M, 418.34459.

Oxidation of Lactols 16 and 17 with PCC. To the lactols (21 mg) in dichloromethane (5 ml) containing Celite, PCC (33 mg) was added. The reaction mixture was stirred for 4 h and worked up as described for the oxidation of lactol acetate **5**. The curde product (18 mg) was subjected to preparative TLC with a 5:1 benzene–diethyl ether to give a crystalline lactone **18** (7 mg, 34%). The lactone was recrystallized from acetone–methanol. Mp 267—272 °C. ^{1}H NMR (90 MHz) 0.70 (3H, s, 18-H), 1.28 (3H, s, 19-H), 4.37 (1H, d, J=13.3 Hz, 4a-H), 4.92 (1H, d, J=13.3 Hz, 4a-H), 5.91 (1H, s, 6-H); MS (70 eV) m/z (rel intensity) 414 (M^+, 100), 355 (29.9), and 341 (19.3) and 206 (74.3). Found: m/z 414.31295. Calcd for $C_{27}H_{42}O_3$: M, 414.31335. IR 1719 cm^{-1} (lactonic C=O), and 1652 (α, β-unsaturated C=O).

The Photolysis of the Hypoiodite of 4,4-Dimethylcholest-5-en-3α-ol (19) in the Presence of Lead Tetraacetate and Iodine. The 3β-ol **19** (100 mg, 0.24 mmol) in benzene (15 ml) containing lead tetraacetate (321 mg, 0.73 mmol) and iodine (194 mg, 0.73 mmol) was irradiated for 3.5 h as described above for cholesterol. The reaction mixture was worked up as usual. The product was subjected to preparative TLC with 10:1 benzene–diethyl ether to give two fractions. The more mobile fraction (21 mg) was again subjected to preparative TLC to give a gummy lactol **20** (4 mg). ^{1}H NMR (90 MHz) 0.69 (3H, s, 18-H), 0.93 (3H, s, 19-H), 1.26 and 1.52 (3H, s, 4a *gem*-dimethyl), 4.87 (1H, br.s, 3-H), 5.39 (1H, m, 6-H); IR 3340 cm^{-1} (OH), and 1042; MS (70 eV) m/z (rel intensity) 412 ($[M-H_2O]^+$, 100), 394 (32.5), and 379 (20.8). Found: m/z 412.36934 $(M-H_2O)^+$. Calcd for $C_{29}H_{48}O$: M, 412.37044.

The less mobile fraction (44 mg) was a mixture of gummy lactol acetates **21**—**24** which were found to be actually a mixture of four possible stereoisomers by its ^{1}H NMR spectrum. ^{1}H NMR (270 MHz) 0.67 an 0.70 (each s, 18-H of the stereoisomers), 1.20 (s, 19-H), 2.49 and 1.58 (each s, 4a *gem*-dimethyl), 2.038, 2.045, 2.048, 2.065, 2.273, 2.098 (each s, OAc attached to C-3 and C-7 of the stereoisomers), 4.95—5.29 (m, 6-H and 7-H of the stereoisomers), 5.66—6.02 (m, 3-H of the stereoisomers); IR 1733 cm^{-1} (OAc), 1237 and 1011 (-O); MS (70 eV) *m/z* (rel intensity) 515 ($[M-Me]^+$, 1.6), 470 ($[M-AcOH]^+$, 14.7), 428 (33.0), 370 (34.5), and 43 (100).

The Transformation of Lactol Acetates 21—24 into Lactone 25. To lactol acetates (30 mg) in toluene (4 ml) cooled by Dry Ice, DIBAL solution (1 M solution, 0.11 ml, Ventron) was added through micro syringe. The solution was stirred for 2 h and worked up in a usual manner. The crude lactols were dissolved in dichloromethane containing Celite and to this solution PCC (15 mg) was added. The solution was stirred for 2 h at room temperature and filtered. The filtrate was washed with water and then brine and dried over anhydrous sodium sulfate. The usual work-up gave a crude lactone which was purified by means of preparative TLC with 1:1 benzene–diethyl ether to give 4 mg of lactone **25**.

Catalytic Reduction of 2,2-Dimethylcholest-4-en-3-one 28. Enone **28** (280 mg) in ethanol (15 ml) containing Pd–C (30 mg) was placed in a round-bottomed flask and was stirred in an atmosphere of hydrogen for 6 h at room temperature. After the removal of the catalyst and the solvent the residue was recrystallized from methanol–acetone to yield 2,2-dimethyl-5*β*-cholestan-3-one (**30**), mp 79.5—81.0 °C. ^{1}H NMR (90 MHz) 0.68 (3H, s, 18-H), 0.99 (3H, s, 19-H), 1.05 and 1.19 each 3H, each s, *gem*-dimethyl), 1.97 (1H, dd, J=3.6 and 15.7 Hz, 4*β*-H), and 2.93 (1H, dd, J=14.3 and 15.7 Hz, 4*α*-H); IR 1706 cm^{-1} (C=O); MS (70 eV) *m/z* (rel intensity) 414 (M^+, 100), 396 (55.4), 381 (51.4), and 259 (54.0). Found: C, 83.96; H, 12.22%. Calcd for $C_{29}H_{50}O$: C, 83.99; H, 12.15%.

The combined filtrates from the recrystallization was collected and after the removal of the solvent the residue was subjected to preparative TLC to give an isomeric ketone **29** identical with the authentic specimen.[12] The ratio of the yields of ketones **29** and **30** in this catalytic hydrogenation was 3:17.

Reduction of 2,2-Dimethyl-5*β*-cholestan-3-one (30) with Sodium Borohydride. The 3-ketone **30** (200 mg) in ethanol (20 ml) containing $NaBH_4$ (200 ml) was stirred for 2 h at room temperature. After the addition of water, the solution was extracted with dichloromethane. The solution was washed with water and then brine, and dried over anhydrous sodium sulfate. After the usual work-up, the crude 3-ols **31** and **32** were recrystallized from methanol. Mp 97.5—98.5 °C. ^{1}H NMR (270 MHz) 0.64 (3H, s, 18-H), 0.89 and 0.91 (each s, 19-H of 3*α*-ol and 3*β*-ol), 0.95 and 0.99 (each 3H, each s, *gem*-dimethyl), and 3.35—3.41 (1H, m, 3*α*- and 3*β*-H); IR 3300 cm^{-1} (OH), 1070, and 1022 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 416 (M^+, 12), 398 ($[M-H_2O]^+$, 100), 383 (41.9), 328 (86.6), 316 (32.5), 243 (50.3), and 95 (15.1). Found: (C, 83.83; H, 12.42%).

The Photolysis of the Hypoiodite of 2,2-Dimethyl-5*α*-cholestan-3*β*-ol (32) in the Presence of Lead Tetraacetate and Iodine. The 3*β*-alcohol (100 mg, 0.24 mmol) in benzene (15 ml) containing lead tetraacetate (321 mg, 0.73 mmol) and iodine (184 mg, 0.73 mmol) was irradiated for 2.5 h as described for the photolysis of cholesterol. After the usual work-up, the product was subjected to preparative TLC with a 10:1 benzene–diethyl ether to give two fractions. The more mobile fraction (31 mg) was gummy lactol acetate **34**. ^{1}H NMR (90 MHz) 0.66 (3H, s, 18-H), 1.03 (3H, s, 19-H), 1.44 (3H, s, 2-Me), 2.06 (3H, s, OAc), 3.40 (2H, br. s, CH_2I), and 5.88 (1H, br. d, J=9.7 Hz, 4-H); MS (70 eV) *m/z* (rel intensity) ($[M-CH_3COOH]^+$, 0.7), 525 ($[M-CH_3COOH-Me]^+$, 1.7), 459 ($[M-CH_2I]^+$, 11), 413 (29.9), 399 (39.4), and 83 (100). Found: *m/z* 540.28212 $(M-CH_3COOH)^+$. Calcd for $C_{29}H_{49}OI$: M, 540.28292.

The less mobile fraction (31 mg) was a gummy lactol **35** which was recrystallized from acetonitrile. Mp 117—119 °C. ^{1}H NMR (90 MHz) 0.65 (3H, s, 18-H), 1.02 (3H, s, 19-H), 1.23 and 1.29 (each 3H, each s, *gem*-dimethyl), and 5.01 (1H, dd, 4-H); IR 3412 cm^{-1}, 1103, 1030, and 1001; MS (70 eV) *m/z* (rel intensity) 414 ($[M-H_2O]^+$, 39), 399 (25.0), 359 (45.2), 314 (44.8), 201 (41.7), and 83 (100). Found: *m/z* 414.38753 $(M-H_2O)^+$. Calcd for $C_{29}H_{50}O$: M, 414.38613.

The Photolysis of the Hypoiodite of 2,2-Dimethyl-5*β*-cholestan-3*α*- (31) and 3*β*-ol (32) in the Presence of Lead Tetraacetate and Iodine. (a) The mixture of 3*α*- and 3*β*-alcohols, **31** and **32** (77 mg, 0.19 mmol) in benzene (15 ml) containing lead tetraacetate (245 mg, 0.56 mmol) and iodine (141 mg, 0.56 mmol) was irradiated for 2 h as described for an isomeric 5*α*-ol hypoiodite above. After the usual work-up the product was subjected to preparative TLC with 5:1 benzene–diethyl ether to give three fractions. The most mobile fraction (18 mg) was an intractable mixture. The second (15 mg) and the third fractions (39 mg) were found to be identical and was a mixture of two lactols **37** and **38**. The second fraction was most probably the corresponding acetate **36** but it was probably hydrolyzed during its extraction from the TLC plates. The mixture of **37** and **38**. ^{1}H NMR (270 MHz) 0.65 (s, 18-H), 0.67 (s, 18-H of C-4 isomer), 0.91 (s, 19-H), 1.02 (s, 19-H of C-4 isomer), 1.15, 1.19, 1.32 and 1.37 (each s, *gem*-dmethyl of two C-4 isomers), 5.11 (dd, J=2.2 and 8.5 Hz, 4-H), 5.21 (dd, J=5.5 and 5.7 Hz, 4-H of C-4 isomer); 414 ($[M-H_2O]^+$, 40.2), 399 (60.3) 314 (41.6), 259 (45.9), and 43 (100); IR 3390 cm^{-1} (OH) and 1042. Found: *m/z* 414.38450 $(M-H_2O)^+$. Calcd for $C_{29}H_{50}O$: M, 414.38610.

(b) In the Presence of Pyridine. The mixture of 3*α*- and 3*β*-alcohols, **31** and **32** (112 mg, 0.27 mmol) in benzene (17 ml) containing lead tetraacetate (357 mg, 0.81 mmol), iodine (205 mg, 0.81 mmol) and pyridine (0.1 ml) was irradiated for 4 h as described above. After the work-up of the reaction mixture by the usual method, the product was subjected to preparative TLC to give three fractions. The most mobile fraction was a gummy secoaldehyde **39** (30 mg). ^{1}H NMR (270 MHz), 0.66 (3H, s, 18-H), 1.16 (3H, s, 19-H), 1.80 (3H, s, 2-Me), 2.52—2.81 (2H, m, 4-H), 4.70 and 4.86 (each 1H, each s, 2-methylene), and 9.64 (1H, dd, J=3.3 and 0.7 CHO); IR 2705 cm^{-1} (aldehydic CH), 1720 (CHO), and 890 ($C=CH_2$); MS (70 eV) *m/z* (rel intensity) 414 (M^+, 4), 399 ($[M-Me]^+$, 4), 359 (51), 341 (44.9), 315 (76.2), and 57 (100). Found: 414.38752 (M^+). Calcd for $C_{29}H_{51}O$: M, 414.38612.

The second fraction (29 mg) was an intractable mixture. The third fraction (27 mg) was lactols **37** and **38**.

The Photolysis of the Hypoiodite of 5*α*-Androstan-17*β*-ol (40). The 17*β*-ol (100 mg, 0.36 mmol) in benzene (20 ml) containing lead tetraacetate (482 mg, 1.09 mmol) and iodine (276 mg, 1.09 mmol) was irradiated under the conditions as described for cholesterol hypoiodite. The work-up as usual gave a product which was subjected to preparative TLC with a 5:1 benzene-diethyl ether to give three fractions. The most and next mobile fractions were an intractable mixture. The least mobile fraction (25 mg) was lactol **41** which was identical with the authentic specimen.[15]

The Photolysis of the Hypoiodite of Cholesterol in the Presence of (Diacetoxyiodo)benzene. Cholesterol (100 mg) in dry benzene (15 ml) containing (diacetoxyiodo)benzene (166 mg) and iodine (131 mg) was flushed with a nitrogen and irradiated with mercury arc for 4 h. The solution was washed with a 5% aq sodium thiosulfate, aq sodium hydrogencarbonate and water and dried. Evaporation of the solution left a residue which was subjected to preparative TLC with a 4:1 benzene-diethyl ether to give a less polar iodo formate (25 mg, 18%) and a more polar cyclic ether **3** (14 mg, 10%).

Photolysis of the Hypoiodite of 4-Oxa-A-homocholest-5-en-3-ol (10) in the Presence of Mercury(II) Oxide and Iodine. (a) The lactol (238 mg) in dry benzene (35 ml) containing mercury(II) oxide (257 mg), iodine (300 mg) and pyridine (0.3 ml) in a Pyrex vessel was irradiated with a 100-W high pressure mercury arc in an atmosphere of nitrogen for 4.5 h. The photolyzed solution was worked up as described for the photolysis of cholesterol hypoiodite. The crude product (327 mg) was subjected to preparative TLC with 3:1 benzene-hexane to give three fractions. The most mobile fraction (122 mg) was an iodo formate **4** identical with the authentic specimen. The second fraction (35 mg) was identified to be a cyclic ether **3**[2a] by a comparison with the authentic specimen. The third fraction (77 mg) was once purified by preparative TLC to give a pure lactone **13** (60 mg) which was identical with the authentic specimen.

(b) The lactol **10** (41 mg) in dry benzene (5 ml) containing mercury(II) oxide (44 mg) and iodine (52 mg) was subjected to the photolysis under the conditions as described above. The work-up as described above gave iodo formate (30 mg, 56%) and cyclic ether (9 mg, 17%). No lactone **13** was detected in the crude product by TLC.

The Photolysis of the Hypoiodite of 2-Indanol (45) in the Presence of Lead Tetraacetate and Iodine. 2-Indanol **45** (150 mg, 1.11 mmol) in benzene (20 ml) containing lead tetraacetate (1.49 g, 3.35 mmol) and iodine (853 mg, 3.35 mmol) was irradiated for 1.5 h as described for cholesterol. The reaction mixture was worked up as usual. The product was subjected to preparative TLC with 10:1 benzene-diethyl ether to give four fractions. The most mobile fraction (24 mg, 6%) was 1,2-bis[iodomethyl]benzene (**47**) which was recrystallized from hexane. Mp 111—112 °C. IR 1147 and 766 cm^{-1}; ^1H NMR (90 MHz) 4.56 (4H, s, CH_2I) and 7.24 (4H, m, aromatic H); MS (70 eV) *m/z* (rel intensity) 358 (M^+, 3.4%), 231 ($[M-I]^+$ 100), and 104 ($[M-2I]^+$, 85.9).

The next mobile oily fraction (64 mg) was a mixture of 1:5:5 mixture of iodo aldehyde **48**, 2-indanol formate (**52**) and 2-(iodomethyl)benzylacetate (**49**) judged from the ^1H NMR. ^1H NMR (90 MHz) Iodo aldehyde **48**: 3.80 (2H d, J=1.8 Hz, CH_2CHO), 4.38 (2H, s, $-CH_2I$), and 9.77 (1H, t, J=1.8 Hz, CHO); formate **52**: 3.01 (2H, dd, J=6 and 17 Hz, benzylic H), 3.36 (2H, dd, J=6 and 17 Hz, benzylic H), 5.5—5.8 (1H, m, CHOCHO), and 7.98 (1H, s, OCHO); Iodide **49**: 2.12 (3H, s, OAc), 4.52 (2H, s, CH_2I), 5.21 (2H, s, CH_2-OAc), and 7.31 (4H, m, aromatic H). This mixture was again subjected to preparative TLC with 5:5:1 mixture of benzene-hexane-diethyl ether to give a 1:1 mixture of 2-indanol formate and 2-(iodomethyl)benzylacetate (4 mg). Further separation could not be achieved.

The next fraction (50 mg, 23%) was an oily 3,4-dihydro-2-benzopyran-3-ol acetate (**46**). ^1H NMR (90 MHz) 2.05 (3H, s, OAc), 2.83 (1H, dd, J=4.2 and 16.5 Hz, benzylic H), 3.19 (1H, dd, J=3.5 and 16.5 Hz, benzylic H), 4.83 (2H, d, J=2.2 Hz), 6.33 (1H, t, J=3.5 and 4.2 Hz, acetal-H); IR 1733 cm^{-1} (OAc) and [1220, 1196 and 1131 cm^{-1} (C–O)]; MS (70 eV) *m/z* (rel intensity) ($[M-CH_3COOH]^+$. 93%), and 104 (100 $(CH_2\text{-}\phi\text{-}CH_2]^+$). Found: *m/z* 132.05632 $(M-CH_3COOH)^+$. Calcd for C_9H_8O: 132.05722.

The most polar fraction (58 mg) was a mixture which was subjected to preparative TLC with a 5:5:1 mixture of ethyl acetate-hexane-diethyl ether to give two fractions. The less polar fraction (11 mg, 4%) was a thick liquid 1,2-bis[acetoxymethyl]benzene **50**.[19]

The more polar fraction (25 mg, 12%) was an aldehyde **51**. IR (neat) 2723 cm^{-1} (CHO), 1724 (CHO), 1222 (OAc), and 1027 (C–O); ^1H NMR (90 MHz) 2.04 (3H, s, OAc), 3.77 (2H, d, J=1.8 Hz, CH_2CHO), 5.08 (2H, s, CH_2OAc), 3.35 (4H, m, aromatic H), and 9.72 (1H, t, J=1.8 Hz, CHO); *m/z* 191 ($[M-1]^+$, 0.2), 104 ($[M-OAc-CHO]^+$, 100) (Found: C, 68.92; H, 6.35. Calcd for $C_{11}H_{12}O_3$; C, 68.74; H, 6.29).

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