

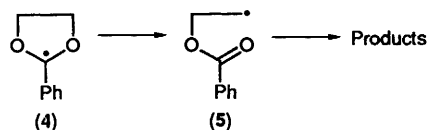
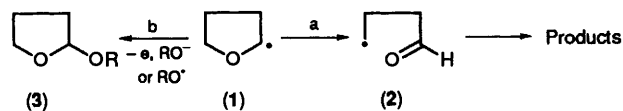
Photoinduced Molecular Transformations. Part 113.¹ One-step Transformations of Cyclic Ethers into ω -Iodoalkyl Formates and of Aldehyde Cyclic Acetals into Monoesters of α,ω -Alkanediols by Iodoxy Radical

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The reaction of cyclic ethers with iodoxy radical and iodine oxide [generated by irradiation of iodine oxide formed *in situ* with red mercury(II) oxide and iodine] gives the corresponding ω -iodoalkyl formates in one step; tetrahydrofuran can be transformed into ω -iodoalkyl formate in 31% yield. Aldehyde cyclic acetals under conditions similar to the reaction of cyclic ethers lead to monoesters of α,ω -alkanediols in one step; cyclohexanecarboxaldehyde ethylene acetal gives 2-hydroxy cyclohexanecarboxylate in 60% yield. The pathways leading to ω -iodoalkyl formates and monoesters of α,ω -alkanediols are discussed based on the results of ¹⁸O-labelling studies with ¹⁸OI and I₂¹⁸O.

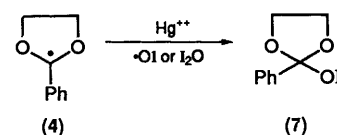
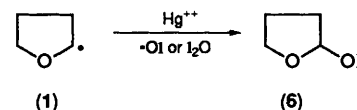
Past studies have indicated that the radicals (1) generated from cyclic ethers, such as tetrahydrofurans, by hydrogen abstraction with oxyl radicals or excited ketones react in either of two directions: radical rearrangements with cleavage of the ring to give isomeric radicals (2) (route a)² or an addition leading to 2-alkoxy- or 2-acyloxy-substituted ethers (3) (route b),³ as outlined in Scheme 1. Radicals (4) generated from aldehyde cyclic acetals under similar conditions, on the other hand, have been reported to react *via* cleavage of the ring to give radicals (5), as outlined in Scheme 2.⁴



In this paper we report that the primary mode of the reaction of the radicals generated from cyclic ethers or cyclic acetals, such as radicals (1) or (4), in the presence of the iodoxy radical and iodine oxide [generated *in situ* from red mercury(II) oxide and iodine] is a combination of the carbon radical with the iodoxy radical or a one-electron oxidation of the carbon radical followed by reaction with iodine oxide and the resulting carbocation to give hypiodites (6) or (7), as outlined in Schemes 3 and 4. Light-induced or thermally induced reactions of these hypiodite (6) or (7) lead to further products arising from a regioselective cleavage of the rings.⁵ Cyclic ethers and aldehyde cyclic acetals can, thus, be transformed into ω -iodoalkyl formates or monoesters of α,ω -alkanediols with the iodoxy radical and iodine oxide in one step, respectively. In the following section, we describe details of these new, synthetically useful reactions.

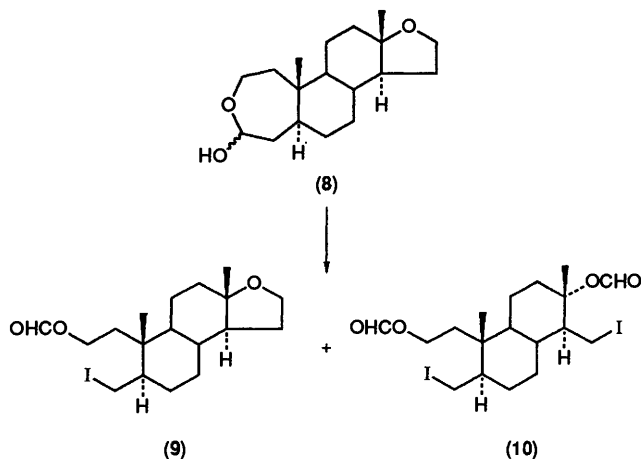
Results

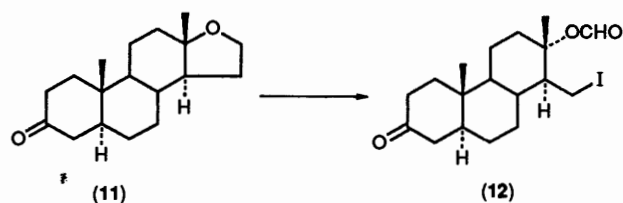
Transformation of Cyclic Ethers into ω -Iodoalkyl Formates.— During our investigation of the transformation of epiandro-



sterone into 3,17-dioxa-5 α -androstane,⁶ we found that irradiation of the hypiodite of lactol (8) in the presence of excess of red mercury(II) oxide and iodine in benzene gave a by-product (10) together with the expected formate (9) (Scheme 5). We then found that irradiation of 17-oxa-5 α -androstan-3-one (11) in benzene containing excess of HgO-I₂ reagent under the conditions mentioned above afforded a 21% yield of iodo formate (12) arising from cleavage of the D-ring (Scheme 6).

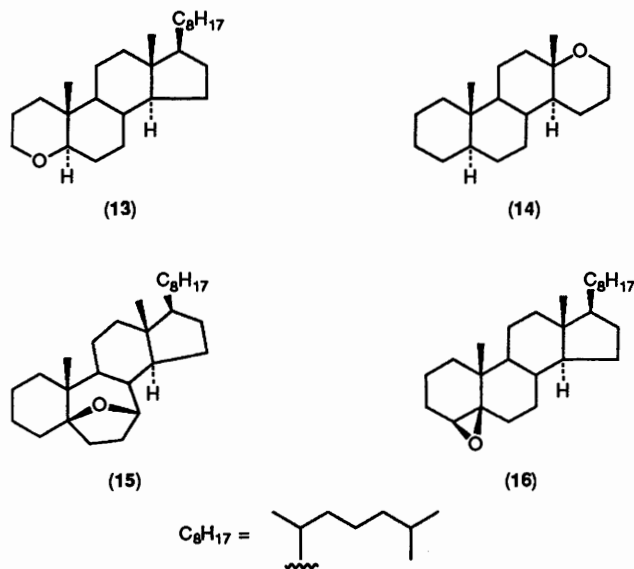
Mechanistic considerations of the cleavage of the ether rings (*vide infra*) to give oxasteroid (11) suggested that this cleavage of the fused tetrahydrofuran (THF) ring may perhaps generally





take place in other cyclic ethers and may be utilized in organic synthesis.

We found that irradiation of 4-oxa-5 α -cholestane (13), D-homo-17 α -oxa-5 α -androstane (14), 5,7 β -epoxy-B-homo-5 β -cholestane (15), and 4 β ,5-epoxy-5 β -cholestane (16) in benzene containing the HgO-I₂ reagent under the above mentioned conditions gave no product analogous to formate (12), and that the starting materials were recovered unchanged.



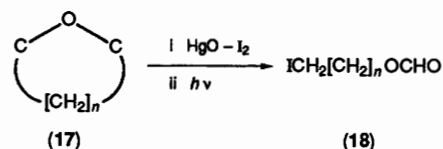
We found, however, that the expected ω -iodoalkyl formates (18a-c) are produced in 15–31% yield when simple monocyclic ethers (17a-c) in benzene containing 3 mol equiv. of red mercury(II) oxide and iodine are irradiated. The results are summarized in Table 1.

Although the yields of ω -iodoalkyl formates are moderate, this new radical reaction gives the iodoalkyl formates in one step from such abundantly available starting materials as tetrahydrofuran (THF) and, therefore, may be of value in organic synthesis.

Transformation of Aldehyde Cyclic Acetals into Monoesters of α,ω -Alkanediols.—Aldehyde cyclic acetals (19) were then subjected to the above mentioned reaction and were found to react in a different manner to compounds (17). Thus, treatment of dodecanal ethylene acetal (19c) in benzene with red mercury(II) oxide and iodine (3 mol equiv. each), followed by irradiation of the resulting solution with a 100-W high-pressure Hg arc [as described for the cleavage of cyclic ethers (17)], resulted in a 67% conversion of the ether and gave a single product (60%) which was identified as the ethylene glycol monoester (20c). Similar treatment of ethylene acetals derived from caproaldehyde, cyclohexanecarbaldehyde, benzaldehyde, and *p*-methoxybenzaldehyde gave the corresponding ethylene glycol monoesters (20a), (20e), (20g), and (20j) in 11–60% yield.

Aliphatic and aromatic aldehyde trimethylene acetals (19d), (19f), (19h), and (19k) were found to react in an analogous

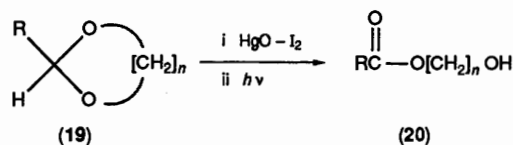
Table 1.



Cyclic ether (17)	Yields of iodo formate (18) (%) ^{a,b}
(a) $n = 2$	31
(b) $n = 3$	30
(c) $n = 4$	15

^a Isolated yield by PLC. ^b Based on the amounts of mercury(II) oxide used.

Table 2.



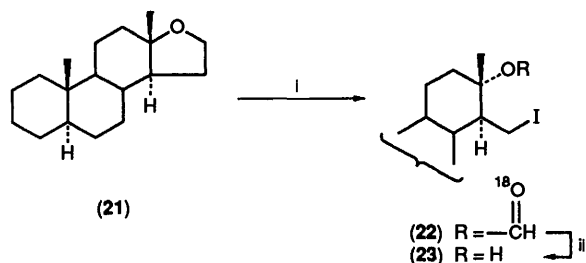
Aldehyde cyclic acetal (19)		Yield (%) of α,ω -diol mono ester (20) ^{a,b}
R	n	
(a) Me[CH ₂] ₄	2	37 (43)
(b) Me[CH ₂] ₄	4	6 (61)
(c) Me[CH ₂] ₁₀	2	60 (33)
(d) Me[CH ₂] ₁₀	3	16 (83)
(e) Cyclohexyl	2	60 (25)
(f) Cyclohexyl	3	19 (64)
(g) Ph	2	11 (75)
(h) Ph	3	52 (28)
(i) Ph	4	16 (17)
(j) <i>p</i> -MeOC ₆ H ₄	2	34 (39)
(k) PhCH ₂	3	27 (46)

^a Isolated yield by PLC. ^b The numerals in brackets are the percentages of the recovered starting material.

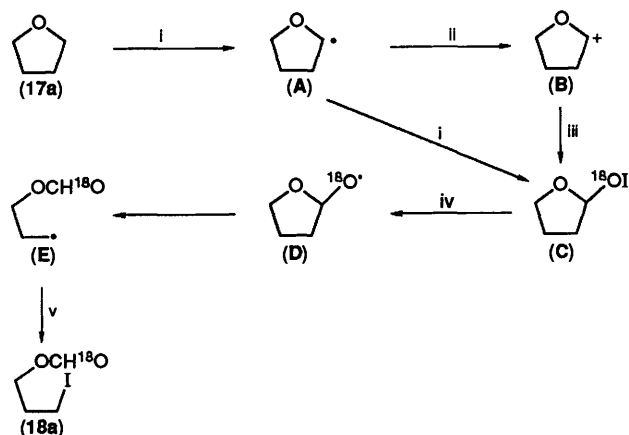
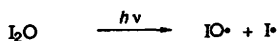
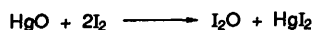
manner and gave the corresponding propane-1,3-diol monoesters (20d), (20f), (20h), and (20k) in 16–52% yield.

Aliphatic and aromatic aldehyde tetramethylene acetals also reacted in an analogous manner, although the yields of the monoesters were low (6–16%). The results are summarized in Table 2.

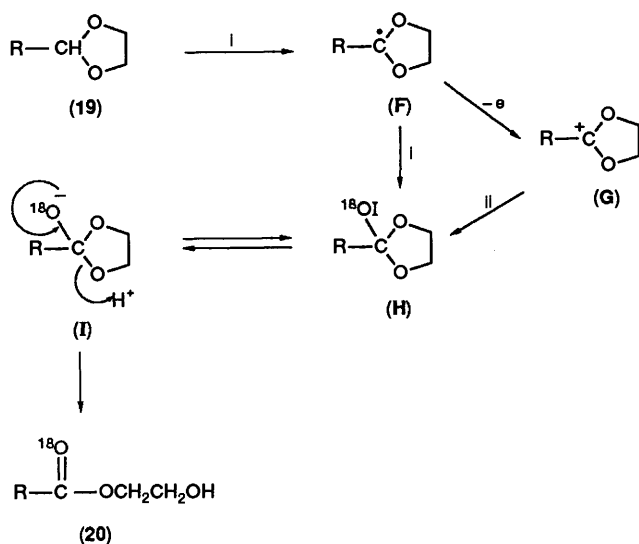
¹⁸O-Labeling Experiments in the Formation of ω -Iodoalkyl Formates from Cyclic Ethers and of Monoesters of α,ω -Alkanediols from Aldehyde Cyclic Acetals.—In order to ascertain the role of the HgO-I₂ reagent in the above mentioned reactions, ¹⁸O-labelling experiments were performed with red mercury(II) oxide labelled with ¹⁸O (¹⁸O, 40 atom%). Irradiation of 17-oxa-5 α -androstane (21) in benzene containing Hg¹⁸O and iodine thus gave 13-formyloxy 15-iodo-D,D-dinor-13,15-seco-5 α -androstane (22) in 21% yield. The mass spectrum of secosteroid (22) confirmed that only one ¹⁸O atom had been incorporated. Analysis of the extent of the incorporation of ¹⁸O into the secosteroid (22) by means of mass spectrometry indicated that ¹⁸O is incorporated in 60% of the product. Reduction of the formate (22) with DIBAL gave the corresponding alcohol (23). Analysis of the incorporation of ¹⁸O into



Scheme 7. Reagents and conditions: i, $\text{Hg}^{18}\text{O}-\text{I}_2$, $h\nu$; ii, DIBAL.



Scheme 8. Reagents and conditions: i, I^{18}O ; ii, Hg^{2+} ; iii, I_2^{18}O ; iv, $h\nu$; v, I_2 .



Scheme 9. Reagents: i, I^{18}O ; ii, I_2^{18}O .

the alcohol (23) showed that no heavy oxygen had been incorporated. This result confirmed that the heavy oxygen in the formate (22) is incorporated in the formyl carbonyl of seco-steroid (22) (Scheme 7).

An ^{18}O -labelling experiment with regard to the formation of α,ω -alkanediol monoesters from aldehyde cyclic acetals was then carried out using phenylacetaldehyde trimethylene acetal (19k) as a typical substrate. Irradiation of acetal (19k) in benzene containing Hg^{18}O (^{18}O , 40 atom%) and iodine gave 3-

hydroxypropyl phenylacetate (20k). Mass spectrometric analysis indicated that one ^{18}O atom had been incorporated into the product (20k) to the extent of 75%.

Discussion

A probable pathway which leads to the ω -iodoalkyl formates is outlined in Scheme 8; the iodoxy radical generated from iodine oxide abstracts a hydrogen attached to the carbon α to the ethereal oxygen of cyclic ether (17a) to give a carbon radical (A) [\equiv (1)]. Lactol hypiodite intermediate (C) is then formed from the carbon radical (A) either by radical combination of (A) with the iodoxy radical or by reaction of a carbocation (B), formed by one-electron oxidation, with iodine oxide. Regioselective β -scission of an alkoxyl radical (D) generated by photolysis gives ω -iodoalkyl formate (18a) via a carbon radical (E). The results obtained in the ^{18}O -labelling experiment are in agreement with this pathway. This formation of ω -iodoalkyl formates from cyclic ethers indirectly confirms the intervention of *iodoxyl* radicals as being the active species formed during irradiation of a solution containing $\text{HgO}-\text{I}_2$.

The foregoing experiments indicated that steroidal 6-membered cyclic ethers do not give ω -iodoalkyl formates. The reason for this is not clear at present, although we consider steric factors to play a role in causing this failure of the cleavage. Our failure to detect any products arising from the cleavage of cyclic ether rings in the reactions of steroidal epoxides (15) and (16) may also be attributable to steric factors.

A plausible pathway leading to monoesters of α,ω -alkanediols is outlined in Scheme 9. Iodoxy radical abstracts a hydrogen attached to the carbon α to the acetal oxygen of aldehyde cyclic acetals (19) to give a carbon radical (F). The formation of a hypiodite (H), directly or through (G), and its ionic cleavage through (I) gives the monoesters of α,ω -alkanediols (20).

The pathway for the reported formation of monoesters of diols from aldehyde cyclic acetals by a treatment with *t*-butyl hydroperoxide in the presence of palladium(II) catalyst⁷ and by treatment with hypochlorous acid in acetic acid-acetone⁸ may be explained similarly.

Experimental

M.p.s were recorded with a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were recorded for Nujol mulls with a JASCO IR 810 infrared spectrophotometer. ^1H NMR spectra were determined with a JEOL JNM-FX 270 spectrometer (270 MHz) (solvent CDCl_3 ; SiMe_4 as an internal standard) (Faculty of Pharmaceutical Sciences of this University). All of the high- and low-resolution mass spectra were recorded with a JEOL JMS-D 300 spectrometer (70 eV) (Faculty of Pharmaceutical Sciences). Preparative TLC (PLC) was carried out on a Merck kieselgel 60 PF₂₅₄.

Reaction of 17-Oxa-5 α -androstan-3-one (11) with Mercury(II) Oxide-Iodine Reagent.—To a solution of oxasteroid (11) (50 mg, 0.18 mmol) in benzene (5 ml) were added red mercury(II) oxide (117 mg, 0.54 mmol) and iodine (138 mg, 0.54 mmol). The solution was flushed with nitrogen and irradiated with a 100-W high-pressure mercury arc for 7 h. The solution was washed successively with aq. 5% sodium hydrogen sulphite, water, and brine, and dried over anhydrous magnesium sulphate. Evaporation of the solvent left a mixture of products, which were subjected to PLC (hexane-ethyl acetate 2:1) to give two fractions. The more mobile fraction (16 mg, 21%) was iodo formate (12), m.p. 94–95 °C (from hexane-ethyl acetate). The less mobile fraction (38 mg, 75%) was the starting material. Compound (12) had ν_{max} (Nujol) 1722 (OCHO), 1710 (C=O),

and 1 202 cm^{-1} ; δ 1.00 (3 H, s, 19- H_3), 1.62 (3 H, s, 18- H_3), 3.32–3.44 (2 H, m, CH_2I), and 8.03 (1 H, s, OCHO); m/z 372 [$(M - \text{HOCHO})^+$, 24.1%] and 245 [$(M - \text{HOCHO} - \text{I})^+$, 100] (Found: C, 51.5; H, 6.5; I, 30.6. $\text{C}_{18}\text{H}_{27}\text{IO}_3$ requires C, 51.68; H, 6.51; I, 30.34%).

Preparation of ω -Iodoalkyl Formates by Irradiation of Monocyclic Ethers with Mercury(II) Oxide–Iodine Reagent. (a) **General Procedure.**—A mixture of THF (5 ml) in dry benzene (20 ml) containing red mercury(II) oxide (1.160 g, 5.37 mmol) and iodine (1.365 g, 5.37 mmol) was irradiated for 8 h under nitrogen. The solution was worked up by the usual procedure. Evaporation of the solvent left ω -iodopropyl formate (**18a**), which was purified by PLC (hexane–ethyl acetate 3:1) to yield pure *iodo ester* (**18a**) [350 mg, 31% based on mercury(II) oxide used], b.p. 72–73 °C (16 mmHg); ν_{max} (neat) 1 727 (C=O), 1 270, and 1 122 cm^{-1} ; δ 2.03–2.32 (2 H, m, CH_2), 3.24 (2 H, t, J 6.82 Hz, CH_2I), 4.25 (2 H, dd, J 6.15 and 5.93 Hz, CH_2O), and 8.06 (1 H, s, OCHO) (Found: M^+ , 213.9466. $\text{C}_4\text{H}_7\text{IO}_2$ requires M , 213.9491).

(b) A mixture of tetrahydropyran (2 ml) in benzene (20 ml) containing red mercury(II) oxide and iodine (5.37 mmol each) was irradiated for 15 h, as mentioned above, to give ω -iodobutyl formate (**18b**) (362 mg, 30%), b.p. 89–90 °C (14 mmHg).

(c) A solution of hexamethylene oxide (oxepane) (180 mg, 1.79 mmol) in benzene (20 ml) containing mercury(II) oxide and iodine (5.37 mmol each) was irradiated for 8 h, as described for the reaction of THF, to give crude ω -iodopentyl formate (**18c**) (68 mg, 15%). This was purified by PLC (hexane–ethyl acetate 3:1) to yield pure *iodo formate* (**18c**).

Preparation of Aldehyde Cyclic Acetals (19).—These acetals were prepared by reaction of the appropriate aldehyde and diols by standard methods. The following ^1H NMR (90 MHz) and mass spectrometric data were recorded.

Dodecanal ethylene acetal (19c). B.p. 94–96 °C (2.5 mmHg); δ 3.90 (4 H, m, $\text{OCH}_2\text{CH}_2\text{O}$) and 4.84 (1 H, t, J 4.10 Hz, OCHO); m/z 228 (M^+ , 0.27%), 227 [$(M - \text{H})^+$, 1.60], and 73 (100) (Found: M^+ , 228.2097. $\text{C}_{14}\text{H}_{28}\text{O}_2$ requires M , 228.2090).

Benzaldehyde ethylene acetal (19g).^{4c} δ 4.00–4.09 (4 H, m, $\text{OCH}_2\text{CH}_2\text{O}$), 5.79 (1 H, s, OCHO), and 7.30–7.48 (5 H, m, Ph); m/z 150 (M^+ , 38.2%), 149 (100), 119 (7.64), and 105 (41.5).

4-Methoxybenzaldehyde ethylene acetal (19j). B.p. 82–83 °C (1.3 mmHg); δ 3.84 (3 H, s, OMe), 4.04 (4 H, d, J 3.3 Hz), and 6.15 (1 H, s, OCHO); m/z 180 (M^+ , 60.0%), 179 [$(M - \text{H})^+$, 78.4], and 73 (100) (Found: M^+ , 180.0792. $\text{C}_{10}\text{H}_{12}\text{O}_3$ requires M , 180.0787).

Hexanal ethylene acetal (19a).^{4d} δ 3.81–3.99 (4 H, m, $\text{OCH}_2\text{CH}_2\text{O}$), and 4.84 (1 H, t, J 4.40 Hz, OCHO); m/z 144 (M^+ , 3.50), 143 [$(M - \text{H})^+$, 34.9], and 93 (100).

Cyclohexanecarbaldehyde ethylene acetal (19e). B.p. 50–51 °C (3 mmHg); δ 3.82 (4 H, m, $\text{OCH}_2\text{CH}_2\text{O}$) and 4.22 (1 H, d, J 4.39 Hz, OCHO); m/z 156 (M^+ , 0.44%), 155 [$(M - \text{H})^+$, 1.09], and 73 (100) (Found: M^+ , 156.1148. $\text{C}_9\text{H}_{16}\text{O}_2$ requires M , 156.1150).

Dodecanal trimethylene acetal (19d). B.p. 115–118 °C (0.35 mmHg); δ 3.60–4.10 [4 H, m, $(\text{OCH}_2)_2$] and 4.48 (1 H, t, J 4.35 Hz, OCHO).

Cyclohexanecarbaldehyde trimethylene acetal (19f). B.p. 61–63 °C (3 mmHg); δ 3.57–4.15 [4 H, m, $(\text{OCH}_2)_2$] and 4.23 (1 H, d, J 4.83 Hz, OCHO); m/z 170 (M^+ , 0.50%), 169 [$(M - \text{H})^+$, 3.7], and 87 (100) (Found: M^+ , 170.1282. $\text{C}_{10}\text{H}_{18}\text{O}_2$ requires M , 170.1307).

Benzaldehyde trimethylene acetal (19h).⁷ δ 3.85–4.30 [4 H, m, $(\text{OCH}_2)_2$] and 5.49 (1 H, s, OCHO); m/z 164 (M^+ , 10.5%), 163 [$(M - \text{H})^+$, 78.4], and 105 (100).

Benzaldehyde tetramethylene acetal (19i).⁷ δ 3.75–3.88 [4 H, m, $(\text{OCH}_2)_2$] and 5.71 (1 H, s, OCHO); m/z 178 (M^+ , 52.4%), 177 [$(M - \text{H})^+$, 23.5], 147 (90.9), and 105 (100).

Phenylacetaldehyde trimethylene acetal (19k).⁹ δ 2.87 (2 H, t, J 5.28 Hz, Ph CH_2), 3.60–4.23 [4 H, m, $(\text{OCH}_2)_2$], and 4.70 (1 H, t, J 5.28 Hz, OCHO); m/z 178 (M^+ , 0.36%), 177 [$(M - \text{H})^+$, 1.53], 163 (14.9), 91 ($\text{C}_6\text{H}_5\text{CH}_2^+$, 32.3), and 87 (100).

Hexanal tetramethylene acetal (19b). B.p. 57–58 °C (3 mmHg); δ 3.55–3.88 [4 H, m, $(\text{OCH}_2)_2$], and 4.65 (1 H, dd, J 5.27 and 5.05 Hz, OCHO); m/z 172 (M^+ , 0.21%), 171 [$(M - \text{H})^+$, 1.1], and 101 (100) (Found: M^+ , 172.1492. $\text{C}_{10}\text{H}_{20}\text{O}_2$ requires M , 172.1463).

Preparation of Monoesters of Alkanediols by Irradiation of Aldehyde Cyclic Acetals (19) with Mercury(II) Oxide and Iodine.

(a) **General Procedure.**—Dodecanal ethylene acetal (**19c**) (300 mg, 1.32 mmol), red mercury(II) oxide (850 mg, 3.95 mmol), and iodine (1 000 mg, 3.95 mmol) in dry benzene (20 ml) were irradiated for 4.5 h, as described for the reaction of THF. The product was subjected to PLC (hexane–ethyl acetate 5:1) to give 2-hydroxyethyl dodecanoate (**20c**) (192 mg, 60%), m.p. 26–28 °C (from MeOH) and recovered starting material (100 mg, 33%); **compound (20c)** showed ν_{max} 3 392 and 3 312 (OH), 1 732 (C=O), 1 374, and 1 176 cm^{-1} ; δ 2.34 (2 H, dd, J 7.48 and 7.03 Hz, CH_2CO_2), 3.80 (2 H, dd, J 4.18 and 5.05 Hz, $\text{OCH}_2\text{CH}_2\text{OH}$), and 4.20 (2 H, dd, J 4.17 and 5.06 Hz, $\text{OCH}_2\text{CH}_2\text{OH}$); m/z 245 [$(M + 1)^+$, 8.84%], 183 [$(M - \text{OCH}_2\text{CH}_2)^+$, 61.41], and 43 (100) (Found: M^+ , 244.2047. $\text{C}_{14}\text{H}_{28}\text{O}_3$ requires M , 244.2038).

Hydrolysis of the monoester (**20c**) with methanolic sodium hydroxide by the standard method gave lauric (dodecanoic) acid, m.p. 43–44 °C, identical with an authentic specimen.

(b) Caproaldehyde ethylene acetal (**19a**) was subjected to cleavage under the conditions mentioned above to give a product. It was subjected to PLC (hexane–ethyl acetate 3:1) to give the starting material (43%) and *monoester (20a)* (37%), ν_{max} (neat) 3 412 (OH), 1 731 (C=O), 1 382, and 1 177 cm^{-1} ; δ 4.18 (2 H, t, CH_2OCO) and 3.78 (2 H, m, $\text{CH}_2\text{CH}_2\text{OCO}$); m/z 161 [$(M + 1)^+$, 8.69%], 143 [$(M + 1 - \text{H}_2\text{O})^+$, 11.3], 99 [$(M - \text{OCH}_2\text{CH}_2\text{OH})^+$, 28.3], and 43 (100) [Found: $(M + 1)^+$, 161.1176. $\text{C}_8\text{H}_{17}\text{O}_3$ requires $(M + 1)$, 161.1178].

(c) Cyclohexanecarbaldehyde ethylene acetal (**19e**) similarly gave a product, which was subjected to PLC (hexane–ethyl acetate 2:1) to give the starting material (25%) and *monoester (20e)* (60%), ν_{max} (neat) 3 380 (OH), 1 716 (C=O), 1 387, and 1 136 cm^{-1} ; m/z 172 (M^+ , 0.82%), 129 (100), and 111 [$(M - \text{OCH}_2\text{CH}_2\text{OH})^+$, 68.9] (Found: M^+ , 172.1093. $\text{C}_9\text{H}_{16}\text{O}_3$ requires M , 172.1099).

(d) Benzaldehyde ethylene acetal (**19g**) (200 mg, 1.33 mmol) in dry benzene (20 ml) containing red mercury(II) oxide and iodine (4.0 mmol each) was irradiated for 3 h. The product was purified by PLC to give the starting material (149 mg, 75%) and *ethylene glycol monobenzoate (20g)* (25 mg, 11%), ν_{max} (neat) 3 412 (OH), 1 700 (C=O), 1 317, and 1 270 cm^{-1} ; δ 3.94 (2 H, t, J 4.62 Hz, $\text{OCH}_2\text{CH}_2\text{OH}$) and 4.64 (2 H, dd, J 4.83 and 4.39 Hz, $\text{OCH}_2\text{CH}_2\text{OH}$) (Found: M^+ , 172.1093. $\text{C}_9\text{H}_{16}\text{O}_3$ requires M , 172.1099).

(e) *p*-Methoxybenzaldehyde ethylene acetal (**19j**) in benzene was irradiated with mercury(II) oxide and iodine (3 mol equiv. each), as mentioned above. The starting acetal (77 mg, 39%) and *monoester (20j)* (67 mg, 34%) were obtained; *ester (20j)* showed ν_{max} (neat) 3 416 (OH), 1 706 (C=O), 1 248, and 1 075 cm^{-1} ; δ 3.90 (5 H, m, CH_2OH and OMe) and 4.43 (2 H, dd, J 5.05 and 4.18 Hz, CH_2OCO); m/z 196 (M^+ , 15.2%), 152 (9.04), and 135 [$(M - \text{OCH}_2\text{CH}_2\text{OH})^+$, 100] (Found: M^+ , 196.0717. $\text{C}_{10}\text{H}_{12}\text{O}_4$ requires M , 196.0735).

(f) Cyclohexanecarbaldehyde trimethylene acetal (**19f**) in benzene was irradiated with red mercury(II) oxide and iodine (3 mol equiv. each) for 4 h to give the starting material (64%) and *monoester (20f)* (19%), ν_{max} (neat) 3 334 (OH), 1 722 (C=O), 1 453, and 1 057 cm^{-1} ; δ 3.68 (2 H, t, J 5.93 Hz, CH_2OH) and 4.22 (2 H, t, J 6.15 Hz, CH_2OCO); m/z 187 [$(M + 1)^+$, 5.13%],

168 [($M - H_2O$)⁺, 2.88], 129 (71.74), and 83 (100) (Found: M^+ , 186.1280. $C_{10}H_{18}O_3$ requires M , 186.1256).

(g) Benzaldehyde trimethylene acetal (**19h**) (200 mg) under similar conditions gave 3-hydroxypropyl benzoate (**20h**) (113.5 mg, 52%) and the starting acetal (56.5 mg, 28%); compound (**20h**) showed ν_{\max} (neat) 3 354 (OH), 1 717 (C=O), and 1 277 cm^{-1} ; δ 3.78 (2 H, t, J 6.15 Hz, OCH_2) and 4.48 (2 H, t, J 6.15 Hz, CH_2OCO); m/z 181 [($M + 1$)⁺, 0.40%], 162 [($M - H_2O$)⁺, 0.97], 123 (74.5), and 105 (100) (Found: M^+ , 180.0763. $C_{10}H_{13}O_3$ requires M , 180.0786).

(h) Phenylacetaldehyde trimethylene acetal (**19k**), prepared in 70% yield by the reaction of phenylacetaldehyde (50% in diethyl phthalate) with an excess of propane-1,3-diol in benzene containing a catalytic amount of toluene-*p*-sulphonic acid under reflux for 10 h, was similarly subjected to reaction to afford the monoester (**20k**). Recovered starting material (92 mg, 46%) and the monoester (**20k**) (59 mg, 27%) were obtained; the latter compound showed ν_{\max} (neat) 3 374 (OH), 1 718 (C=O), 1 454, and 1 278 cm^{-1} ; δ 3.63 (2 H, s, CH_2CO_2), 3.78 (2 H, t, J 6.15 Hz, CH_2OH), and 4.48 (2 H, t, J 6.15 Hz, OCH_2); m/z 194 (M^+ , 7.8%), 123 (74.0), 105 (100), and 91 [($C_6H_5CH_2$)⁺, 92.2%] (Found: M^+ , 194.0914. $C_{11}H_{14}O_3$ requires M , 194.0943).

(i) The reaction of caproaldehyde tetramethylene acetal (**19b**) (300 mg) similarly gave recovered acetal (61%) and butane-1,4-diol monoester (**20b**) (21 mg, 6.4%), ν_{\max} (neat) 3 296 (OH), 1 716 (C=O), and 1 166 cm^{-1} ; δ 3.68 (2 H, t, J 5.93 Hz, CH_2OH) and 4.10 (2 H, t, J 6.15 Hz, CH_2OCO); m/z 189 [($M + 1$)⁺, 2.1%], 99 [($M - OCH_2CH_2CH_2CH_2OH$)⁺, 81.6] and 43 (100) [Found: ($M + 1$)⁺, 189.1490. $C_{10}H_{21}O_3$ requires ($M + 1$)⁺, 189.1491].

(j) Reaction of benzaldehyde tetramethylene acetal (**19i**) (200 mg), as mentioned above, gave the recovered acetal (17%), a small amount of $PhCO_2CH_2CH_2CH_2CHO$, and monoester (**20i**) (16%), ν_{\max} (neat) 3 420 (OH), 1 718 (C=O), and 1 274 cm^{-1} ; δ 3.73 (2 H, t, J 5.28 Hz, CH_2OH) and 4.37 (2 H, t, J 5.49 Hz, CH_2OCO); m/z 194 (M^+ , 1.1%), 176 [($M - H_2O$)⁺, 0.73], 123 (57.6), and 105 [($M - OC_4H_8OH$)⁺, 100] (Found: M^+ , 194.0924. $C_{11}H_{14}O_3$ requires M , 194.0943).

¹⁸O-*Labelling Experiment in the Transformation of 17-Oxa-5 α -androstane (21) into the ω -Iodoalkyl Formate (22) with Hg¹⁸O and I₂ under Irradiation.*—Oxasteroid (**21**) (25 mg, 0.057 mmol) was dissolved in dry benzene (5 ml) containing Hg¹⁸O (¹⁸O, 40 atom%) (105 mg, 0.29 mmol) and iodine (124 mg, 0.29 mmol) and was irradiated under nitrogen for 6 h. Work-up of the solution gave a crude product which was subjected to PLC (3:1 hexane-ethyl acetate) to give the starting material (10 mg, 40%) and ω -iodoalkyl formate (**22**) (8 mg, 21%), ν_{\max} ($CHCl_3$) 1 719 (C=O), 1 386, and 1 208 cm^{-1} ; δ (270 MHz) 0.77 (3 H, s, 18-H), 1.59 (3 H, s, 19-H₃), 3.36 (2 H, d, J 3.66 Hz, CH_2I), and 8.04 (1 H, s, $OCHO$); FD-MS m/z 406 (M^+ for labelled compound, 12.15%) and 404 (M^+ for unlabelled compound, 31.40).

The iodoalkyl formate, m.p. 70–71 °C (from hexane), corresponding to product (**22**) obtained by using ordinary mercury(II) oxide, was also analysed by mass spectrometry: {Found: (EI-MS) ($M - HOCHO$)⁺, 358.119. ($C_{18}H_{29}IO_2 - HOCHO$)⁺ requires m/z , 358.1155. (FD-MS) m/z 404 (M^+ , 34.25%), 406 [($M + 2$)⁺, 2.60], and 359 [($M - OCHO$)⁺, 100]}.

The calculated incorporation of ¹⁸O into the formate (**22**) based on these mass spectrometric results was 60%.

Reduction of ¹⁸O-Incorporated Iodoalkyl Formate (22) with DIBAL.—Reduction of formate (**22**) with DIBAL by a standard procedure gave the corresponding alcohol (**23**), m.p. 115–117 °C (from hexane-ethyl acetate); ν_{\max} ($CHCl_3$) 3 530 (OH), 1 382, and 1 217 cm^{-1} ; δ (90 MHz) 0.76 (3 H, s, 19-H), 1.22 (3 H, s, 18-H), and 3.44 (2 H, d, J 2.85 Hz, CH_2I); m/z 249 [($M - I$)⁺, 18.0%] and 231 [($M - I - H_2O$), 100] [Found: ($M - I$)⁺, 249.2214. ($C_{17}H_{29}IO - I$) requires m/z , 249.2216].

¹⁸O-*Labelling Experiment in the Transformation of Phenylacetaldehyde Trimethylene Acetal (19k) into 3-Hydroxypropyl Phenylacetate (20k) with Hg¹⁸O and I₂ under Irradiation.*—Cyclic acetal (**19k**) was transformed into the corresponding phenylacetate (**20k**) with Hg¹⁸O (¹⁸O, 40 atom%) and I₂ by the procedure described above. EI-MS; 196 (M^+ for deuteriated product, 0.72%) and 194 (M^+ for non-deuteriated product, 1.57). The diol phenylacetate (**20k**) obtained by using ordinary mercury(II) oxide was analysed by mass spectrometry. EI-MS; 194 (M^+ , 7.78%) and 196 [($M + 2$)⁺, 0.2]. The calculated incorporation of ¹⁸O into the ester based on these mass spectrometric data was 75%.

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Paper 0/00428F

Received 29th January 1990

Accepted 24th May 1990