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Photoinduced Molecular Transformations. Part 154.[1] On the Mechanism of the Formation of the 5-Iodopentyl Formate in the Photolysis of Cyclopentanol Hypoiodite in Solution in the Presence of Mercury(II) Oxide-Iodine.

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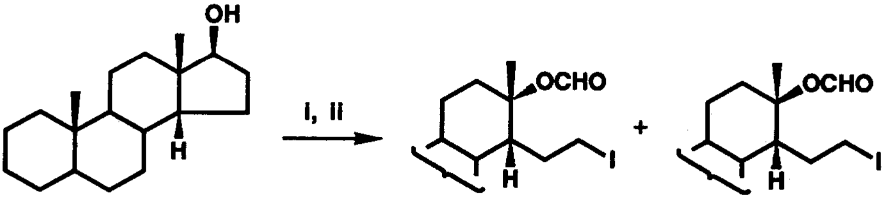
***Abstract*:** ^{18}O-labelling experiments established that the formation of 5-iodopentyl formate in the photolysis of cyclopentanol hypoiodite in the presence of excess mercury(II) oxide-iodine in benzene involves the following pathway: a) a β-scission of a cyclopentyloxy radical to rearrange to a primary 5-oxopentyl radical, which generates the corresponding carbocation by a metal ion-assisted one-electron oxidation; b) an intramolecular addition of the 5-oxopentyl cation to the formyl oxygen to generate a tetrahydropyranyl cation; c) a combination of the tetrahydropyranyl cation with diiodine oxide (I_2O) to form a lactol hypoiodite; d) generation of a carbon-centred radical by a selective β-scission of a carbon-carbon bond of an alkoxyl radical generated from the lactol hypoiodite; e) abstraction of an iodine by the carbon-centred radical from an iodine molecule to form the 5-iodopentyl formate. 5-Iodopentyl formate is also produced by prolonged irradiation of a solution of 5-iodopentanal in the presence of mercury(II) oxide and iodine in benzene with Pyrex-filtered light. The formate in this case should be formed through the generation of the 5-oxopentyl cation (mentioned above) by mercury-assisted ionization of its carbon-iodine bond, followed by the same pathway as that mentioned above.

We previously reported a new photoinduced radical rearrangement of steroidal homoallyl alkoxyl radicals generated by the photoreaction of hypoiodites of steroidal homoallyl alcohols with excess mercury(II) oxide and iodine in a protic solvent.[2] Our subsequent studies using a variety of substrates have shown that this new reaction takes place exclusively or concomitantly in the reaction of alkoxyl radicals generated by the irradiation of appropriate cyclic alcohol hypoiodites generated by excess mercury(II) oxide-iodine.[3] For example,[4a] the irradiation of a solution of the hypoiodite of 5α-androstan-17β-ol **1** *in situ* generated in benzene containing red mercury(II) oxide and iodine (each 3 mol equiv.) with Pyrex-filtered light gave a mixture of stereoisomers of 16-iodo-17-nor-13,17-seco-5α-androstan-13α- and 13β-yl formates, **2** and **3**, as the principal products arising from this new rearrangement of the corresponding alkoxyl radical, as outlined in Scheme 1. The photolysis of the hypoiodites of cyclopentanol **7** gave rise to 5-iodopentyl formate **9**, corresponding to formates **2** and **3**, as the major products with an accompanying formation of 5-iodopentanal **8**[8] and a cyclopentyl tetrahydropyranyl ether **10** in low yields, as outlined in Scheme 2.[4a] No products corresponding to the formates, **2** and **3**, were formed in the photolysis of the hypoiodites of cyclic alcohols generated by lead tetraacetate and iodine.[5]

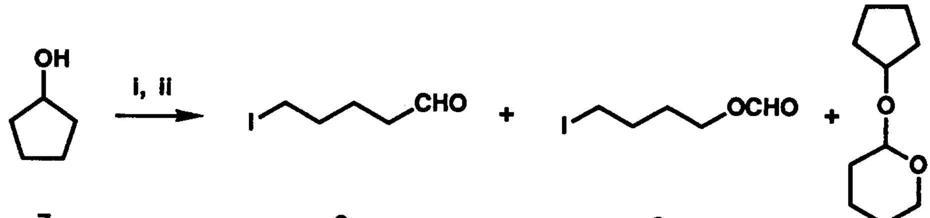
Subsequent ^{18}O-labelling studies[4] concerning the pathway for the formation of the formates, **2** and **3**, using ^{18}O-labelled mercury(II) oxide disclosed that the oxygen atom of the mercury(II) oxide is specifically transferred to the formyl group of the ester. This result suggested that the formation of the formates involved the following sequence: (a) a selective β-scission of the alkoxyl radical **A**, which rearranges to a stabilized tertiary carbon-centred radical **B** having a carbonyl group; (b) a subsequent one-electron oxidation of the carbon-centred radical **B** to the corresponding stabilized tertiary carbocation **C**; (c) its intramolecular combination with the formyl oxygen to form a tetrahydropyranyl cation **D**; (d) its reaction with diiodine oxide (I_2O) to generate a lactol hypoiodite **E**; and (e) a regioselective β-scission of the carbon-carbon bond of an alkoxyl radical **F** generated



1 **2** **3**

I, HgO - I_2, benzene; II, hν

Scheme 1



7 **8** **9** **10**

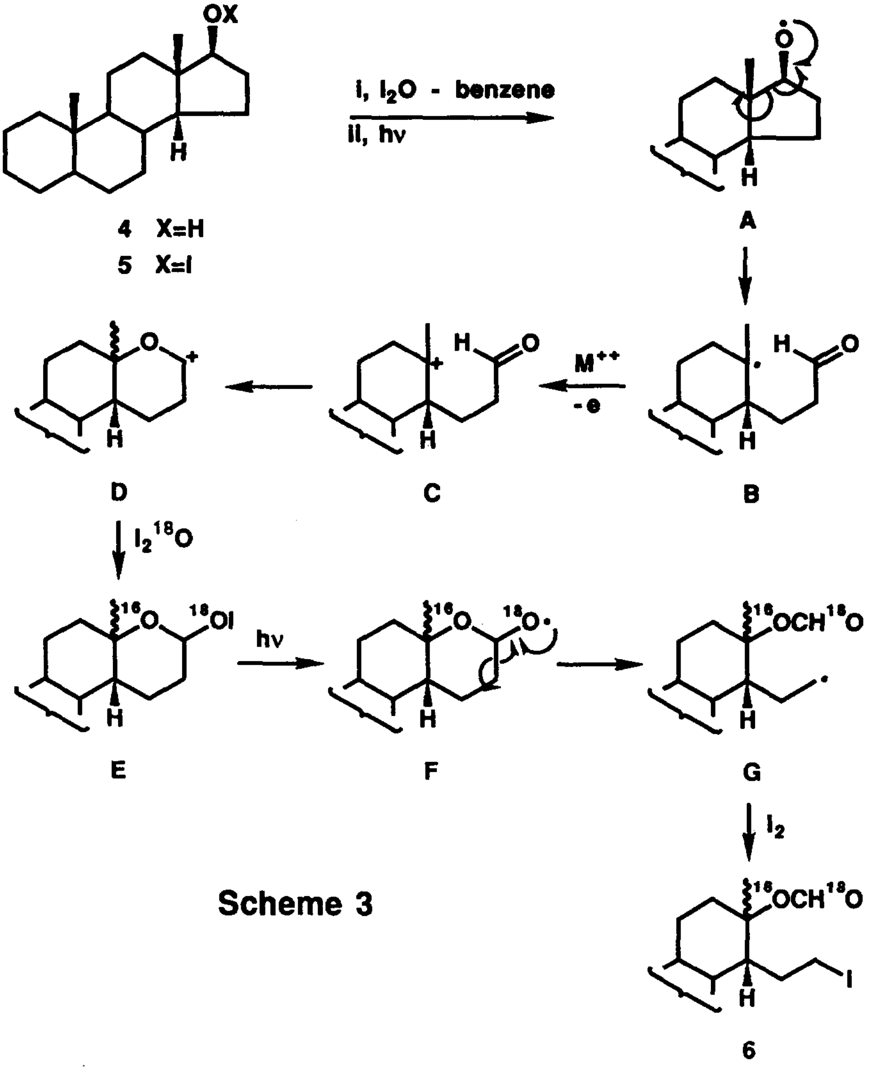
I, HgO - I_2, benzene; II, hν

Scheme 2

from the hypoiodite, followed by the abstraction of an iodine from an iodine molecule by the resulting carbon-centred radical G to form the observed iodo formates, **2** and **3** (Scheme 3). The last process – the formation of the iodo formate in the photolysis of lactol hypoiodites in the presence of mercury(II) oxide and iodine – was shown independently by us[6] and found to be very useful in organic synthesis.[6,7] The 5-iodopentyl formate **9** produced from cyclopentanol **7** was then reasonabley assumed to be formed through the pathway outlined in Scheme 3.

An alternative mechanism has, however, recently been claimed for the formation of 5-iodopentyl formate **9** in the hypoiodite photolysis of cyclopentanol **7**.[9] Thus, Courtneidge reported that the photolysis of the hypoiodite of cyclopentanol **7** in the presence of yellow or red mercury(II) oxide in either CCl_4 or benzene gave our products **8**, **9**, and **10** together with new products, δ-valerolactone **11** and 1,4-butandiol monoformate **12** (Scheme 4), and that subjection of the 5-iodopentanal **8** to the above-mentioned reaction conditions over a period of 4h gave formate **9** and lactone **11**.[10] Based on these results and the results of a GLC analysis of the product composition *versus* the time course of the reaction of the photolysis of cyclopentanol hypoiodite, he claimed[9] that 5-iodopentyl formate **9** is formed from the first-formed 5-iodopentanal **8** rather than the pathway outlined in Scheme 3 proposed by Suginome and colleagues.[4] He claimed that a Baeyer-Villiger-type oxidation was probably responsible for this aldehyde – formate transformation, since when octanal as a model substrate was exposed to the above-mentioned reaction conditions for 26h (time considerably longer than that required for the formation of 5-iodopentyl formate **9**) octyl formate was obtained in 19% yield. He did not mention, however, the species responsible for this oxidation.[9,11]

It is apparent that his claimed pathway fails to explain the formation of iodo formates, **2** and **3**, from the steroidal substrate **1** outlined in Scheme 1, since: (a) it can not accommodate the result obtained from our ^{18}O-



Scheme 3

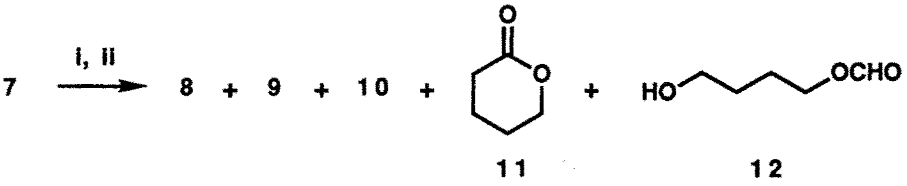
labelling experiment outlined in Scheme 3, and (b) the claimed path must require the formation of a primary carbon-centred radical, rather than a stabilized tertiary carbon-centred radical **B** in a β-scission of the first-formed alkoxyl radical **A** outlined in Scheme 3. Needless to say, (a) the exclusive formation of a tertiary carbon-centred radical arising from a β-scission of the C(13)-C(17) bond over a primary carbon-centred radical arising from a cleavage of the C(16)-C(17) bond in the photolysis of steroidal 17β-ol nitrites is a well-established fact;[12] (b) the formation of both 13α- and 13β-yl formates, **2** and **3**, requires a cleavage of the C(16)-C(17) bond in the photolysis of the corresponding hypoiodite (Scheme 1).

Thus, we further scrutinized the pathway of the 5-iodopentyl formate formation in order to clarify whether his claimed pathway is specifically operative in cyclopentanol hypoiodite photolysis. We have thus undertaken: (a) a product analysis of the photolysis of cyclopentanol hypoiodite under the reported conditions;[9] (b) ^{18}O-

labelling experiments of the photolysis using $Hg^{18}O$; and (c) the photolysis of 5-iodopentanal under the conditions of cyclopentanol photolysis. We describe here in full the results of our experiments, which exclude the pathway claimed by Courtneidge and confirm our original methanism.

RESULTS AND DISCUSSION

Products in the Photolysis of the Hypoiodite of Cyclopentanol 7 in the Presence of Mercury(II) Oxide and Iodine. ———Table 1 summarizes our results under his reported conditions together with those reported by Courtneidge. The major product in the present experiment (runs 1-4) was 5-iodopentanal **8** (28-65%), together with 5-iodopentyl formate (4-7%), 1,4-diiodobutane **13** (4-6%), and ω-iodopentanoic acid **14** (1-12%) as the minor products, regardless of whether red or yellow mercury(II) oxide in CCl_4 or benzene was used, as outlined in Scheme 5. On the other hand, Courtneidge obtained only a trace to 5% of 5-iodopentanal **8** and neither 1,4-diiodobutane **13** nor ω-iodopentanoic acid **14** (runs 6-8). The yellow form of mercury(II) oxide is finer and is known to be more reactive than the red form.[14] Our results indicate that a more reactive yellow form gives lower yields of 5-iodopentanal **8** and higher combined yields of three products; **9**, **13**, and **14** [*e.g.* **8**; 49.8%. **9** plus **13** plus **14**; 21.6% (run 1). **8**; 28.0%. **9** plus **13** plus **14**; 24.2% (run 3)]. Our results suggest that the first-formed 5-iodopentanal **8** is transformed into products **13** and **14**, and part of formate **9** by the secondary reactions (*vide infra*). The lower yield of 5-iodopentanal **8** recorded in our previous paper[4a] is probably due to this secondary reaction.



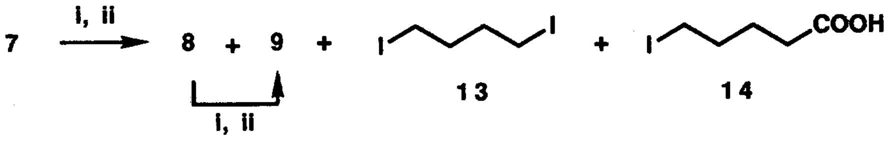
11 12

i, HgO - I_2, benzene or CCl_4
ii, hν

Scheme 4

We were unable to reproduce his results, which showed a rather wide variation in the products and their yields for his three combinations of the reagents (red or yellow HgO) and solvents (run 6-8, Table). The deviation of our results with those reported by Courtneidge is probably due to a difference in the concentration of the substrate, the reaction scale, and the method of product isolation, which are not mentioned in his communication. The deviation may also be due to the nature of the reaction, which is more or less of a heterogeneous type. In any event, in view of our own results, the material balance of 98% in benzene (run 6) involving the formation of δ-valerolactone **11** and the effects of the solvent for the yields of the products reported by him are remarkable.

Photoinduced Transformation of 5-Iodopentanal 8 into 5-Iodopentyl Formate 9 in the Presence of Mercury(II) Oxide-Iodine in Benzene.——We then examined the photolysis of 5-iodopentanal **8** under the conditions of the photolysis of cyclopentanol **7** (mentioned above) in order to confirm whether 5-iodopentyl formate **9** is formed



i, HgO - I_2, benzene or CCl_4
ii, hν

Scheme 5

Table

The Products and Isolated Yields in Photolysis of Cyclopentanol Hypoiodites in Solution in the Presence of HgO – I_2

Run		Yield (%)							Ref.	
	Products HgO / solvent	8	9	10	11	12	13	14		
1	red / benzene	49.8	7.0	0	0	0	3.5	11.1	This work	(a)
2	red / CCl_4	64.9	4.3	0	0	0	5.9	1.4	〃	(a)
3	yellow / benzene	28.0	8.6	0	0	0	4.1	11.5	〃	(a)
4	yellow / CCl_4	58.7	4.0	0	0	0	3.9	5.2	〃	(a)
6	red / benzene	(trace) 5	(1) 40	(trace) 5	(0.5) 43	(trace) 5	0	0	Ref. 9	(a)
7	red / CCl_4	(1)	(1.5) 26	0	(1.2)	trace	0	0	〃	(a)
8	yellow / CCl_4	(1) trace	(trace) trace	(1) 49	(1) 5	0	0	0	〃	(a)
5	red / benzene	8	16	7	0	0	0	0	Ref. 4a	(b)

(a) Substrate / HgO / I_2 ; 1 / 3 / 2.6 mol equiv. hν, 1.5h

(b) Substrate / HgO / I_2 ; 1 / 3 / 3 mol equiv. hν, 7h

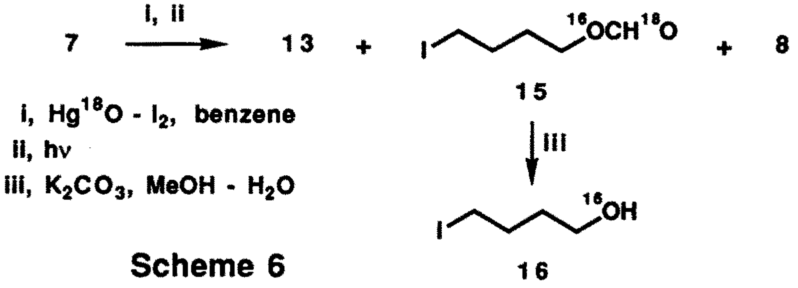
The numbers in the bracket are molar ratios. No yields are given.

from the aldehyde **8**; the photolysis of 5-iodopentanal **8** in benzene containing HgO (3 equiv.) and I_2 (2.6 equiv.) in an atmosphere of nitrogen for 4 h, followed by the usual work-up gave, in fact, 5-iodopentyl formate **9** in 20%

yield, confirming the transformation of aldehyde **8** into formyl ester **9** when the solution is exposed to light for a long time (Scheme 5).

The photolysis of octanal under the conditions reported by Courtneidge was also repeated; the photolysis of octanal in the presence of yellow mercury(II) oxide (3 equiv.) and I_2 (2.6 equiv.) in CCl_4 for 4 h under nitrogen gave a crude recovered aldehyde, the ^1H NMR spectrum of which exhibited no signal assignable to a formyl proton, proving the absence of the corresponding formyl ester in the recovered material.

The ^{18}O Labelling Experiments on the Formation of 5-Iodopentyl Formate 8 in the Photolysis of Cyclopentanol Hypoiodite in the Presence of $Hg^{18}O$-I_2.——The ^{18}O-labelling experiment was carried out using a freshly prepared yellow mercury(II) oxide containing 20.25% of ^{18}O (3 equiv.) and iodine (2.6 equiv.) in benzene under the conditions mentioned above to give 1,4-diiodobutane **13** (2.4%), 5-iodopentyl formate **15** (11.2%) and 5-iodopentanal **8** (25.1%). We found that the disappearance of the starting cyclopentanol **7** was faster when yellow mercury(II) oxide, rather than red mercury(II) oxide, was used. No 5-iodopentanoic acid **14** was obtained in this experiment. An analysis of the 5-iodopentyl formate **15**, obtained above, by mass spectrometry indicated that 19.33% of the ^{18}O was incorporated into the formate **15**, and that the formate containing two atoms of ^{18}O was less than 1%.



Scheme 6

A mild hydrolysis of the 5-iodopentyl formate **15** with potassium carbonate in aq. methanol at room temperature for 1 h resulted in a 85% conversion of the formate and gave 4-iodobutanol **16** (79% yield), which contained 6.59% of ^{18}O-alcohol (mass spectrometry). The results thus implied that the starting 5-iodopentyl formate **15** comprised $ICH_2CH_2CH_2CH_2{}^{16}OCH^{18}O$ (12.74 %), $ICH_2CH_2CH_2CH_2{}^{18}OCH^{16}O$ (6.59%), plus $ICH_2CH_2CH_2CH_2{}^{16}OCH^{16}O$ (80.67 %),

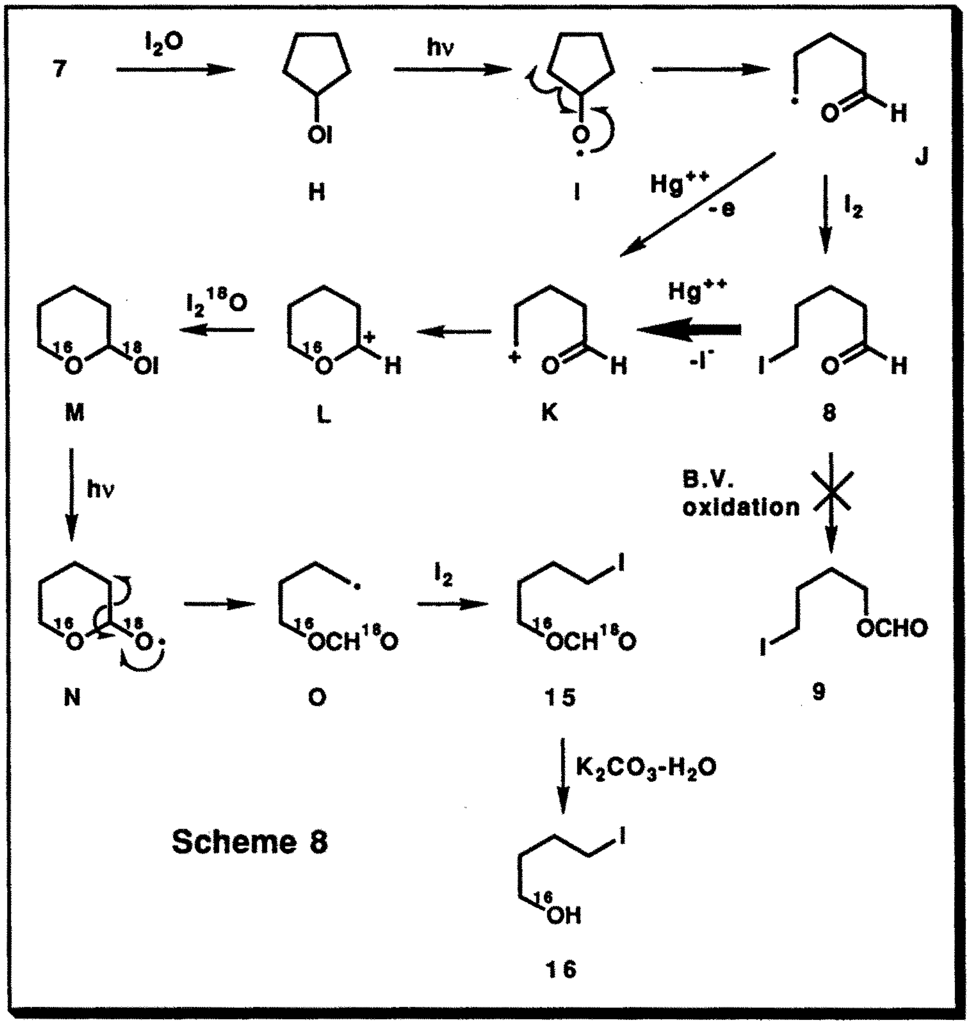
The Pathway for the Formation of 5-Iodopentyl Formate in the Photolysis of Cyclopentyl Hypoiodite in Solution containing Mercury(II) Oxide-Iodine.——The foregoing experiments concerning the pathway for the formation of 5-iodopentyl formate in the photolysis of cyclopentanol hypoiodite in the presence of excess mercury(II) oxide-iodine in benzene established that 5-iodopentyl formate **9** is formed *via* the path essentially originally suggested by Suginome and coworkers using a steroidal substrate.[4] The pathway for the formation of formate **15** is outlined in Schemes 7 and 8.

The reactive species generated from mercury(II) oxide and iodine here should be diiodine oxide (I_2O).

$$Hg^{18}O + 2I_2 \longrightarrow I_2{}^{18}O + HgI_2$$

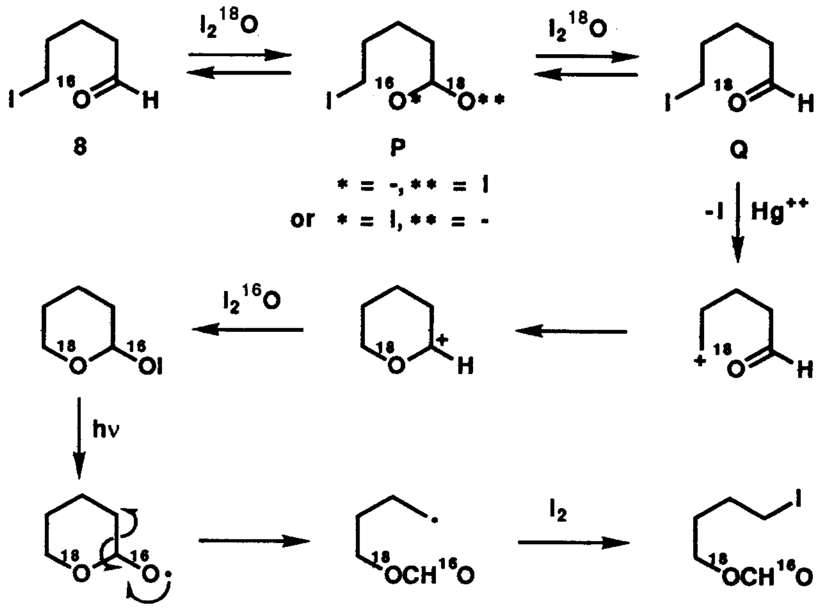
$$I_2{}^{18}O + 2ROH \longrightarrow 2ROI + H_2{}^{18}O$$

Scheme 7

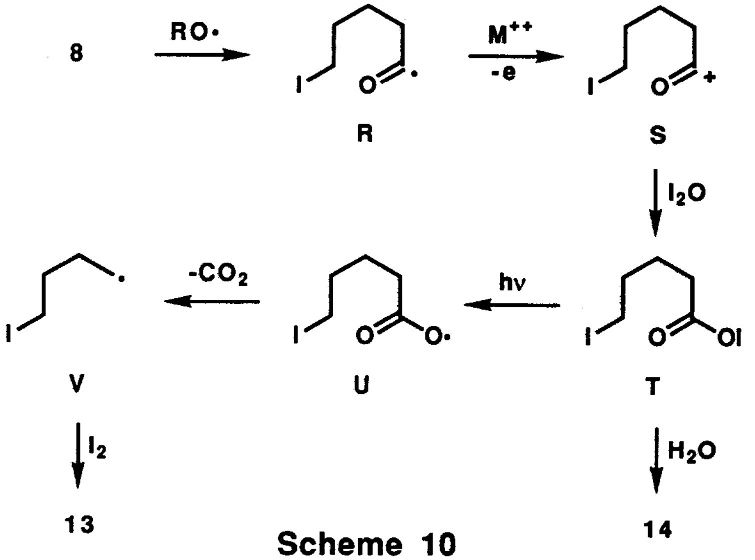


Scheme 8

Although I_2O is not isolable, its involvement is certain, since isolable Br_2O was formed by an analogous reaction of HgO and Br_2.[13,14] The corresponding hypoiodite was then formed by the reaction of cyclopentanol with I_2O (Scheme 7). The cyclopentanoxyl radical **I** photochemically generated from cyclopentanol hypoiodite **H** rearranged to a primary 5-oxopentyl radical **J**, which reacted competitively in two directions: (a) a conversion to the corresponding carbocation **K** by a metal ion-assisted one-electron oxidation and (b) the formation of 5-iodopentanal **8** by the abstraction of iodine from an iodine molecule (Scheme 8). In contrast to the primary radical



Scheme 9



Scheme 10

J, the aforementioned steroidal tertiary radical B, arising from a fused cyclopentanoxyl radical A (Scheme 3), is exclusively converted to the tertiary carbocation C, and then the tetrahydropyranyl cation D, since the formation of the iodide by the reaction of the tertiary radical C with iodine should be extremely slow. An intramolecular combination of the 5-oxopentyl cation K with the formyl oxygen then generates a tetrahydropyranyl cation L which reacts with diiodine oxide, I_2O, to give a lactol hypoiodite M. The photochemical generation of a new alkoxyl radical N, followed by a selective β-scission of its carbon-carbon bond then affords 4-formyloxybutyl radical O. It finally captures iodine to give the observed 5-iodopentyl formate 15.

The ^{18}O-labelling experiments described in the foregoing part disclosed that the ^{18}O in 5-iodopentyl formate 15 was incorporated mostly to the formyl oxygen of the ester group. This result excludes the pathway for the formation of formate 16 claimed by Courtneidge[9] since the claimed formation of the formate 15 *via* a Beayer-Villiger-type oxidation of aldehyde 8 requires an insertion of oxygen to the non-formyl oxygen of the ester group. A control experiment using octanal also excludes the claimed pathway, since the photolysis of the octanal under the conditions of the cyclopentanol hypoiodite photolysis indicated that no corresponding formate was formed. 5-Iodopentyl formate 9 should then be formed *via* a metal ion-catalyzed generation of the 5-oxopentyl cation K from 5-iodopentanal, followed by the path outlined in Scheme 8. (L→M→N→O→15). The mercury-assisted cleavage of the C-X bond of alkyl halides to form the corresponding carbocation is a textbook reaction which was investigated a half century ago.[15] The diiodine oxide and a metal ion in the presence of excess mercury(II) oxide-iodine should thus interplay with the radical intermediates throughout the present hypoiodite photolysis.[16]

The ^{18}O labelling experiments also showed that the 5-iodopentyl formate contained 6.59% of $I(CH_2)_4{}^{18}OCH^{16}O$. The formation of this labelled formate is outlined in Scheme 9; the oxygen of 5-iodopentanl 8 is scrambled by the reaction with $I_2{}^{18}O$ *via* a tetrahedral species P to give ^{18}O-aldehyde Q, from which $ICH_2CH_2CH_2CH_2{}^{18}OCH^{16}O$ is formed through the sequence outlined in Scheme 9. One of the present authors has already reported an example of the scrambling mechanism involving an intermediate corresponding to species P.[4b]

A Probable Pathway of the Formation of 1,4-*Diiodobutane* 13 *and ω-Iodopentanoic Acid* 14 *in the Photolysis of Cyclopentyl Hypoiodite in Solution containing Mercury(II) Oxide-Iodine.*——One of the probable pathways leading to the formation of 1,4-diiodobutane 13 and ω-iodopentanoic acid 14 is outlined in Scheme 10. Hydrogen abstraction from 5-iodopentanal 8 by the alkoxyl radical generates a carbonyl radical R which is oxidized to a species S by a metal ion. The reaction of species S with diiodine oxide gives acyl hypoiodite T, from which ω-iodopentanoic acid is recovered. On the other hand, a photoinduced Hunsdiecker-type reaction through the generation of radicals U and V gives 1,4-diiodobutane 13. There are precedents[16] for this process in which alkyl halides are formed by the thermal decarboxylation of acyl hypoiodite.

EXPERIMENTAL

The IR spectra were determined for Nujol mulls with a JASCO IR 810 infrared spectrometer. The ^1H NMR spectra were determined in $CDCl_3$ ($SiMe_4$ as internal reference) with JEOL JNM EX-270-FT high-resolution spectrometer operated at 270 MHz (unless stated otherwise). The *J*-values are in Hz. High- and low-resolution mass spectra were recorded with a JEOL JMS-DX 303 mass spectrometer (70 eV) at the Faculty of Pharmaceutical Sciences of this University. PLC was carried out on Merck silica gel 60 PF_{254}.

General Procedure for the Photolysis of the Hypoiodite of Cyclopentanol 7 in the Presence of Red or Yellow Mercury(II) Oxide and Iodine.——Cyclopentanol (300 mg, 3.49 mmol) in benzene (30 cm^3) or CCl_4 (30 cm^3) containing red or yellow mercury(II) oxide (2267 mg, 10.47 mmol) and iodine (2302 mg, 9.07 mmol) was irradiated with a 100-W high-pressure Hg arc through a Pyrex-filter in a nitrogen atmosphere for 1.5 h (under the reaction conditions reported in Reference 9). The solution was filtered, and the filterate was then washed with 5% $Na_2S_2O_3$, water, and brine successively and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave a residue which was subjected to PLC (benzene-silica gel) to give four products **13**, **8**, **9**, and **14** in the order of their mobility. The products yields in each photolysis were as follows:

(a) *The reaction in the Presence of Yellow Mercury(II) Oxide in Benzene.*——**13** (43.8 mg), **8** (68.3 mg), **9** (207.5 mg), and **14** (91.4 mg).

(b) *The reaction in the Presence of Red Mercury(II) Oxide in Benzene.*————**13** (38 mg), **8** (56 mg), **9** (368 mg), and **14** (88 mg).

(c) *The reaction in the Presence of Yellow Mercury(II) Oxide in CCl$_4$.*————**13** (42 mg), **8** (31.8 mg), **9** (434 mg), and **14** (41.5 mg).

(d) *The reaction in the Presence of Red Mercury(II) Oxide in CCl$_4$.*————**13** (64 mg), **8** (34 mg), **9** (480 mg), and **14** (11 mg).

The Photolysis of Octanal in the Presence of Red Mercury(II) Oxide - Iodine in CCl$_4$————A solution of octanal (461 mg, 2.59 mmol) in CCl_4 (30 cm^3) containing red HgO (2340 mg, 3 eq. mol) and I_2 (2376 mg, 2.6 eq. mol) was irradiated for 4 h (as mentioned above). The work-up of the solution (as mentioned above) gave a crude product. Its ^1H NMR spectrum exhibited no signal at δ 8.06 assignable to the OCHO group of octyl formate.

Preparation of Yellow Hg^{18}O.————This mercury(II) oxide containing ^{18}O was freshly prepared by the reaction of a solution of $HgCl_2$ in water containing 20.25% of $H_2{}^{18}O$ with NaOH as described previously.[4a, 13]

The ^{18}O Labelling Experiments on the Formation of 5-Iodopentyl Formate 15 in the Photolysis of Cyclopentanol Hypoiodite in the Presence of Hg^{18}O - I$_2$.————A solution of cyclopentanol (114 mg, 1.33 mmol) in benzene (11 cm^3) in the presence of yellow mercury (II) oxide (865 mg, 3.99 mmol) containing 20.25 % of $Hg^{18}O$ and iodine (880 mg, 3.47 mmol) was flashed with nitrogen and irradiated for 1.5 h under nitrogen. The usual work-up of the solution gave a residue from which three products (1,4-diiodobutane **13** (10 mg, 2.4%), 5-iodopentyl formate **15** (33.7 mg, 11.2%), and 5-iodopentanal **8** (70.4 mg, 25.1%)) were isolated by PLC (benzene). The analysis of the incorporation of ^{18}O to formate **15** by mass spectrometry indicated that the formate contained 19.33% of $I(CH_2)_4{}^{16}OCH^{18}O$, $I(CH_2)_4{}^{18}OCH^{16}O$ plus $I(CH_2)_4{}^{18}OCH^{18}O$. The $I(CH_2)_4{}^{18}OCH^{18}O$ was less than *ca.* 5% in all of the heavy oxygen-incorporated formates.

Hydrolysis of ^{18}O-5-Iodopentyl Formate.————A solution of ^{18}O-5-iodopentyl formate **15** (30.5 mg, 0.134 mmol) and potassium carbonate (20 mg) in methanol (5 cm^3) and water (0.5 cm^3) was stirred for 1 h at room temperature. Evaporation of the solvent gave a residue which was extracted with diethyl ether. The organic layer was washed with water and then brine, and dried over anhydrous Na_2SO_4. Removal of the solvent gave a residue which was subjected to PLC (benzene) to give the starting formate **15** (4.5 mg, 15%) as a more mobile fraction and 4-iodobutanol **16** (18 mg, 79% based on the converted formate). An analysis of the incorporation of ^{18}O by mass spectrometry indicated that the 4-iodobutanol contained 6.59% of $I(CH_2)_3CH_2{}^{18}OH$.

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10 One of the handwritten curves drawn by a broken line in the Figure in his communication[9] should not represent 2-(cyclopentyloxy)tetrahydropyrane **10** as he described, but δ-valerolactone **11**, since the former can not be formed from 5-iodopentanol **8** under the reaction conditions described by him. A probable genesis of this lactone **11** from 5-iodopentanal would be through a disproportionation of intermediate N (Scheme 8). A probable genesis of this lactone **11** in the photolysis of cyclpentanol hypoiodite would be through a cyclization of ω-iodopentanoic acid **14** in a GLC column during the course of its isolation if he used preparative GLC for the isolation. Preparative TLC is a safer technique for the isolation.

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