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SYNTHESIS AND REACTIONS OF SOME TETRACYCLIC LACTONES OF THE BICYCLO[2.2.1]HEPTANE SYSTEM

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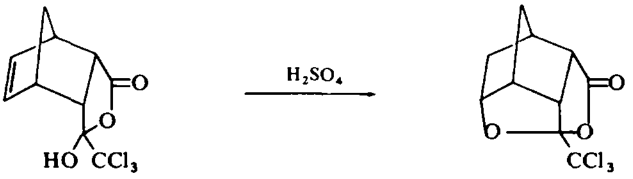
Abstract—A series of 9-*exo*-halo tetracyclic lactones was prepared through the reaction of chlorine, bromine and iodine in aqueous sodium bicarbonate with *endo-cis*-3-trichloroacetylbicyclo[2.2.1]hept-5-ene-2-carboxylic acid lactol (**1**). Reaction of **1** with peracetic acid formed the corresponding hydroxy derivative. Addition of bromine to lactol **1** in carbon tetrachloride gives exclusively the *exo-cis*-dibromide addition product. Hydrolysis of chloro and bromo tetracyclic lactones **3** and **4** with 5% sodium hydroxide gives *endo-cis*-5,6-dihydroxybicyclo[2.2.1]heptane-2,3-dicarboxylic acid dilactone (**11**). Reaction of iodo derivative **5** with one or two equivalents of sodium hydroxide gives dilactone **11**; but with 5% sodium hydroxide the product is *endo*-cis-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid anhydride (**16**). Reaction of **5** with sodium iodide in acetone gives lactol **1**, anhydride **16**, and starting material. The mechanistic implications are discussed.

RECENTLY we reported that in the presence of cold concentrated sulfuric acid, trichloromethyl lactol **1** is smoothly converted to tetracyclic lactone **2**.[1]



1 **2**

This result provided for the first time experimental evidence that the OH group was directed under the bicyclic ring of **1**, as the study of models had already indicated. The ease by which this reaction proceeded prompted us to investigate the possible synthesis of a series of 9-*exo* substituted derivatives of **2** through reactions initiated by electrophilic attack at the double bond. The behaviour of this series under hydrolytic conditions would also provide an interesting comparison with a similar system recently reported upon Moriarty and Adams.[2] Of particular interest we report an unusual elimination in the case of the 9-*exo*-iodo derivative **5** and an example of a *cis* addition of bromine to a double bond.

Treatment of lactol **1** with chlorine, bromine, or iodine in aqueous methanolic sodium bicarbonate solution resulted in an immediate rapid reaction accompanied by the precipitation of crystalline tetracyclic lactone **3**, **4** or **5**. The reactions were

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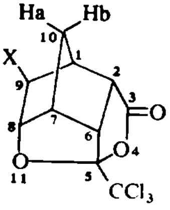
essentially complete after about 10 minutes and over 80% yields were obtained. The corresponding hydroxy derivative **6** was prepared by heating a methylene chloride solution of lactol **1** with peracetic acid.



3: X = Cl
4: X = Br
5: X = I
6: X = OH

The elemental analyses, IR, and NMR spectra were entirely consistent with the proposed structures **3–6**. The 5-membered lactone rings gave rise to characteristic IR bands at 1795 cm^{-1}. Hydroxyl group absorption, present in the starting lactol 1 at 3450 cm^{-1} (Nujol, KBr), was completely absent in the products **3–5**. Hydroxyl absorption in compound **6** was sharp at 3580 cm^{-1} (KBr). The NMR spectra are revealing, particularly with respect to the C$_8$-*exo* and C$_9$-*endo* protons, Table 1. The chemical shift and coupling assignments of Table 1 are based upon a detailed NMR analysis of an analogous system having a close similarity to the present series.[3a] The coupling of the C$_8$-*exo* proton with the bridgehead proton at C$_7$, and the W-coupling between the C$_9$-*endo* and C$_{10}$ (*anti*) protons, Hb, are consistent with the proposed structures. As is usual, no coupling was observed between the C$_9$-*endo* proton and the bridgehead proton at C$_1$. The failure to observe coupling between the C$_8$-*exo* and C$_9$-*endo* protons can reasonably be attributed to a dihedral angle close to 90°, caused by the distortion of the bicyclic ring by the oxygen-11 bridge. Similar lack of coupling of vicinal *trans* protons has been reported for other strained cyclic and bicyclic systems.[3a, 3b]

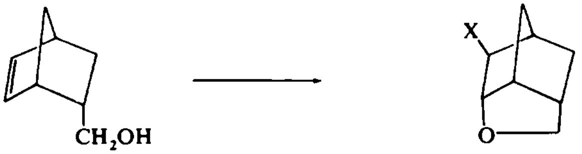
Table 1. NMR data for tetracyclic lactones (Pyridine-d$_5$)

No.	X	*Chemical shifts, τ*		*Coupling constants, Hz*	
		C$_8$-*exo*-H	C$_9$-*endo*-H	$J_{8,7}$	$J_{9,10b}$
		(multiplicity)[a]			
3	Cl	5·17(d)	5·76(d)	5	2
4	Br	4·98(d)	5·69(d)	5	2
5	I	4·83(d)	5·77(d)	5	2·5
6	OH	5·24(–)[b]	5·70(d)	5	—

[a] Multiplicities indicate only gross features. Line broadness or small shoulder lines were occasionally present.

[b] The doublet was not resolved, only a broad single line was observed.

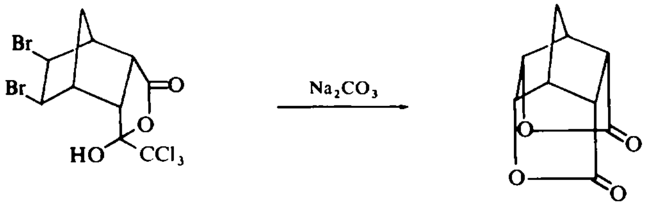
Although participation by neighbouring carboxyl in the bromination of olefins in aqueous base is well documented,[5–10] somewhat less information is available concerning neighbouring OH groups. Winstein and Goodman[11] have reported the conversion of α,α-dimethylallyl alcohol to 1-bromo-2,3-epoxy-3-methylbutane by aqueous sodium hypobromite; but in the case of allyl alcohol itself, OH participation did not occur.[12] Henbest and Nichols[13, 14] have observed that compound **7** rapidly forms tricyclic ether **8** or **9** on treatment with basic perbenzoic acid or mercuric acetate in the presence of chloride ion, respectively. Several other reports of the participation of neighbouring OH groups in the mercuration of olefinic alcohols have recently appeared.[15–18] In our case, the rapid formation of the cyclic ethers without rearrangement on halogenation of lactol **1** clearly indicates that the appropriately placed OH group readily participates in neighbouring group displacements, and thus precludes the possibility of Wagner–Meerwein type rearrangements.[19]



7

8: X = OH
9: X = HgCl

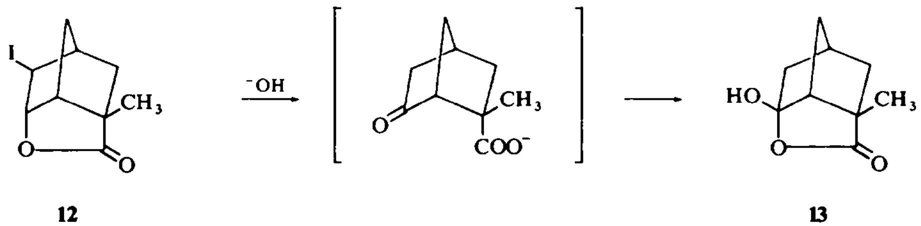
Reaction of lactol **1** with bromine in carbon tetrachloride gave a dibromide of lactol **1**, as indicated by elemental analysis and the presence of IR bands for OH and lactone CO groups. The steric configuration of the dibromide is revealed by the NMR spectrum, which exhibits as significant features two quarters at τ 4·27 and 4·96 (pyridine-d_5), both formed through coupling constants of 2 Hz and 7 Hz. This can only indicate the *exo*-cis configuration shown by structure **10**. The 7 Hz coupling is characteristic of the coupling between two *endo-cis* protons, while the 2 Hz coupling is consistent with the W-coupling between *endo* protons and the anti proton of the methylene bridge.[3, 4, 20, 21] Reaction of the dibromide with aqueous sodium carbonate formed dilacetate **11**, as would be expected from the *exo-cis* geometry of dibromide **10**.



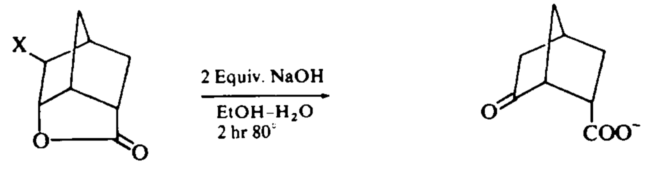
10 **11**

Although several other cases of *cis* brominations have been reported,[22–24] rarely do they proceed with such stereospecificity unaccompanied by rearrangements or competing *trans* addition. Contrasted with the cyclization reactions discussed above, here the *endo* lactol ring must serve merely to promote, by either steric or electronic means, the exclusive *exo-cis* addition.

Beckman and Geiger[25] have shown that iodolactone **12** is converted by aqueous alkali to lactol **13**, presumably by lactolization between the carboxylate and the CO group of a ketone intermediate. Similarly, Moriarty and Adams[2] report that only keto carboxylate **15** is obtained from basic hydrolysis of some related lactones **14**.



12 **13**

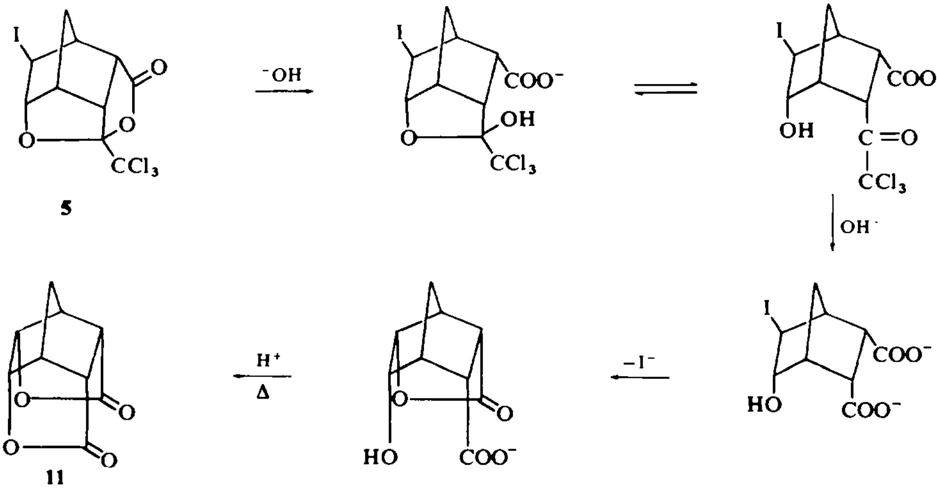


14: X = Br, I, OTs **15**

The mechanism for this conversion was shown to involve initial attack by base on the lactone ring, followed by dehydrohalogenation with a second equivalent of base to give the enol of ketone **15**.[2]

In contrast, tetracyclic lactones **3**, **4** and **5**, which could behave in a similar fashion, instead follow a different path. Iodo-lactone **5**, on heating with one or two equivalents of sodium hydroxide, gives only dilactone **11**. Initial attack would presumably occur at the lactone CO group to give a lactol, which through ring chain tautomerism would be in equilibrium with the open chain trichloromethyl ketone, Scheme 1.

SCHEME 1

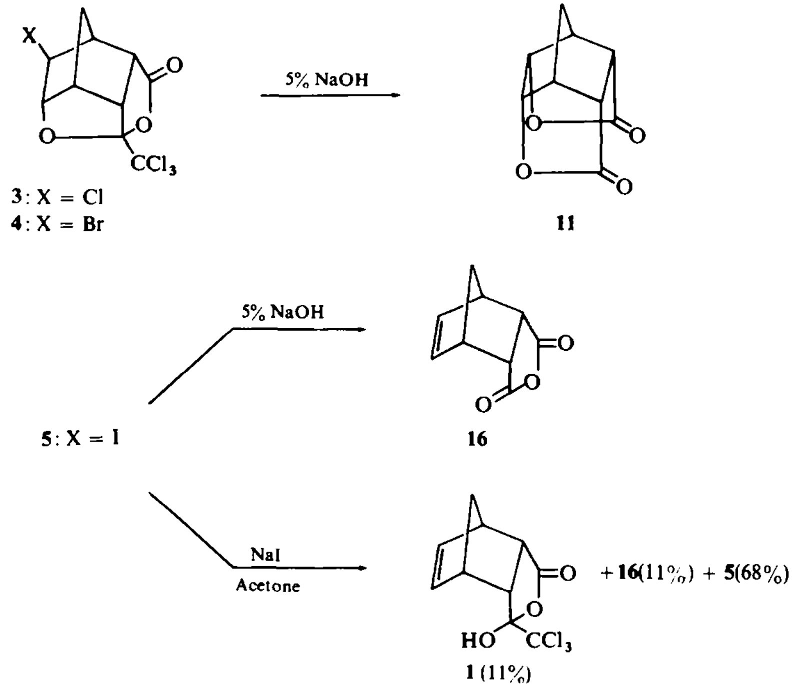


5

11

A second hydrolysis would then give the dicarboxylic acid intermediate. The doubling of the yield of **11** on going from one to two equivalents of sodium hydroxide would indicate that the second hydrolysis proceeds at a faster rate than the first. In the absence of a third equivalent of base, formation of dilactone **11** through neighbouring group displacement is not surprising. In the presence of excess base (5% NaOH) both chloro- and bromo-lactones **3** and **4** also give dilactone **11**, Scheme II. Thus in the presence of the neighbouring carboxylate ion intramolecular displacement of halogen is preferred over dehydrohalogenation leading to ketone.

Scheme 2



For iodo lactone **5** an entirely different behaviour is observed on treatment with 5% sodium hydroxide. In this case anhydride **16** was the only product isolated. Apparently nucleophilic attack on iodine with accompanying elimination occurs in preference to either neighbouring group displacement or dehydrohalogenation. When iodo lactone **5** was treated with sodium iodide in acetone, trichloromethyl lactol **1** and anhydride **16** were both isolated along with starting material. In the absence of iodide ion only starting material was recovered.

Formation of lactol **1** can be accounted for only by an elimination initiated by nucleophilic attack of iodide ion on the iodine of iodolactone **5**. Concerted elimination of the trichloromethyl anion can then account for the formation of anhydride **16**. Nucleophilic attack on halogen is not often observed, but occasional instances of such behaviour have been reported.[26,27]

Although in the conversion of lactol **1** to compounds **3–5** there is a distinct possibility of a Wagner–Meerwein rearrangement, so often encountered in bicyclic systems, the conversion of **3–5** to known compounds having unrearranged structures precludes any such transformations. The rapid participation of the neighbouring hydroxyl group and the increase in ring strain, as suggested by molecular models, would favour non-rearrangement.

EXPERIMENTAL

Elemental analyses were carried out by Galbraith Laboratories, Knoxville, Tennessee. M.ps are uncorrected. IR spectra were recorded on the Beckman IR-8 spectrophotometer. NMR spectra were recorded on the Varian HA-60 spectrometer. *Endo-cis*-3-trichloroacetylbicyclo[2.2.1]hept-5-ene-2-carboxylic acid lactol (**1**) was prepared from the reaction of sodium trichloroacetate with *endo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid anhydride (**16**) in dimethoxyethane.[28] For comparison purposes *endo-cis*-5,6-dihydroxybicyclo[2.2.1]heptane-2,3-dicarboxylic acid dilactone (**11**), lit.[29] mp 274–275°, was prepared by heating *exo-cis*-5,6-dibromobicyclo[2.2.1]heptane-2,3-dicarboxylic acid anhydride in aqueous sodium carbonate.[29]

9-exo-*Chloro-5-trichloromethyl*-4,11-*dioxatetracyclo*$[5.2.1.1^{5,8}.0^{2,6}]$*undecane-3-one* (**3**)

A soln of KCl (5·14 g; 43·2 mmole) in 100 ml 5% $NaHCO_3$ aq was added to a soln of **1** (5·00 g, 18 mmole) in about 60 ml MeOH. The soln was cooled in an ice-water bath and Cl_2 gas was bubbled through, whereupon a white ppt formed almost immediately. After passing Cl_2 through the soln for about 10 min, the solid was filtered and the filtrate was treated with more Cl_2, which caused an additional small amount of white solid to form. Trituration of the solid with sat Na_2SO_3 aq (2 × 10 ml) and then with water (4 × 10 ml), and drying *in vacuo* at 58° gave 4·68 g (14·7 mmole, 83·1%) of white crystals, mp 155·5–156° after several recrystallizations from CCl_4; (Found: C, 37·80; H, 2·45; Cl, 44·96. $C_{10}H_8Cl_4O_3$ requires: C, 37·76; H, 2·54; Cl, 44·60%): $\nu_{C=O}^{KBr}$ 1795 cm^{-1}.

9-exo-*Bromo-5-trichloromethyl*-4,11-*dioxatetracyclo*$[5.2.1.1^{5,8}.0^{2,6}]$*undecane-3-one*. (**4**)

A soln of Br_2 (4·9 g: 31 mmole) and KBr (12·85 g, 108 mmole) in 25 ml $NaHCO_3$ aq was added in one portion with vigorous stirring to a soln of **1** (5·0 g, 18 mmole) in 50 MeOH. A yellow ppt formed immediately and, after about 1 min the soln became too thick to stir. After 1½ hr the solid was collected, triturated with Na_2SO_3 aq (2 × 10 ml), and washed with water (2 × 10 ml). The product, which appeared to be partly inorganic was extracted with 125 ml hot 4:1 $CHCl_3$-CCl_4. Evaporation of the solvent gave **4** (5·5 g: 15·2 mmole, 84·4%). Recrystallization from CCl_4 gave white crystals, mp 141–145°. (Found: C, 33·14; H, 2·19; Br, 21·96; Cl, 29·08. $C_{10}H_8BrCl_3O_3$ requires: C, 33·13; H, 2·23; Br, 22·05; Cl, 29·35%): $\nu_{C=O}^{KBr}$ 1795 cm^{-1}.

9-exo-*Iodo-5-trichloromethyl*-4,11-*dioxatetracyclo*$[5.2.1.1^{5,8}.0^{2,6}]$*undecane-3-one* (**5**)

A soln of I_2 (4·6 g, 36 mmole) and KI (17·9 g, 108 mmole) in 50 ml 5% $NaHCO_3$ aq was added in one portion with vigorous swirling to a soln of **1** (5·0 g, 18 mmole) in 40 ml MeOH. An immediate reaction occurred in which a red-brown solid formed. The flask was placed in the dark and swirled periodically for 0·5 hr. The solid was collected, triturated with 5% $NaHSO_3$ aq (8 × 10 ml), washed with water (5 × 10 ml), and dried *in vacuo* at 50°. Recrystallization from 1:1 $CHCl_3$-CCl_4 and decolorization with charcoal afforded **5** (6·8 g; 16·6 mmole, 92·2%). Recrystallization from CCl_4-$CHCl_3$ aq, then from CCl_4-hexane gave white crystals, mp 151–151·5°. (Found: C, 29·08; H, 2·08; Cl, 25·72; I, 31·21. $C_{10}H_8Cl_3IO_3$ requires: C, 29·32; H, 1·97; Cl, 25·98; I, 30·99%): $\nu_{C=O}^{KBr}$ 1795 cm^{-1}.

9-exo-*Hydroxy-5-trichloromethyl*-4,11-*dioxatetracyclo*$[5.2.1.1^{5,8}.0^{2,6}]$*undecane-3-one*. (**6**)

To a soln of **1** (3·0 g, 10·8 mmole) **1** in 100 ml CH_2Cl_2 was added in one portion 10 ml 40% peracetic acid-acetic acid soln (commercial grade). The mixture was heated at reflux for 63 hr, cooled and poured over 100 g ice. The CH_2Cl_2 layer was separated and washed with 20 ml water, $NaHCO_3$ aq (2 × 10 ml), and water (2 × 20 ml). The water layer was saturated with NaCl and extracted with CH_2Cl_2 (4 × 20 ml). The extracts were washed with $NaHCO_3$ aq (2 × 10 ml) and water (2 × 20 ml). The combined CH_2Cl_2 soln was dried over $MgSO_4$ and the solvent was removed *in vacuo* at less than 30°, to give **6** (2·87 g; 9·56 mmole, 88·5%). Recrystallization from 2:1 $CHCl_3$-CCl_4 gave white crystals mp 196·5–197°. (Found: C, 39·94; H, 3·04; Cl, 35·72. $C_{10}H_9Cl_3O_4$ requires: C, 40·09; H, 3·03; Cl, 35·51%); ν_{max}^{KBr}, cm^{-1}, 3580 sharp (OH), 1795 (C=O).

3-endo-*Trichloroacetyl*-5,6-exo-cis-*dibromo-bicyclo*[2.2.1]*heptane-2-carboxylic acid lactol.* (**10**)

Into a flask equipped with an addition funnel, condenser and stopper were placed **1** (5·00 g; 17·7 mmole) and 150 ml CCl_4. The mixture was heated to reflux and, after the lactol had dissolved, 20 ml of 10% soln of Br_2 in CCl_4 were added in one portion, whereupon crystals formed in the mixture. The mixture was stirred at reflux for 2 hr, allowed to cool to room temp, then stirred at that temp for an additional hr. The crystals were collected and washed with CCl_4. Recrystallization from a 3:1 mixture of CCl_4-$CHCl_3$ yielded 7·15 g (16·1 mmole, 91·0%) of white crystals, mp 199·5–200·5°. (Found: C, 26·98; H, 2·04; Br, 35·98; Cl, 23·90. $C_{10}H_9Br_2Cl_3O_3$ requires: C, 27·09; H, 2·05; Br, 36·04; Cl, 24·00%) ν_{max}^{KBr}, cm^{-1}: 3390 (OH), 1760 (C=O).

Hydrolysis of exo-cis-*dibromo-lactol* (**10**)

A mixture of 10% $NaHCO_3$ aq (50 ml) and **10** (1·00 g; 2·2 mmole) was heated under reflux for 2 hr. The resulting light orange soln was acidified with HCl and extracted continuously with ether. Evaporation of the ether from the extracts did not yield any product, so the water was removed *in vacuo* and the resulting crystals were extracted with CH_2Cl_2, affording 350 mg (1·9 mmole, 86·4%) of tan crystals. Recrystallization from CCl_4-$CHCl_3$ gave white crystals, mp 271–272°; IR spectrum identical with that of an authentic sample of **11**.

Reaction of chloro-lactone 3 *with* 5% *aqueous sodium hydroxide*

Chloro-lactone **3** (600 mg, 1·8 mmole) was heated under reflux for 4 hr with 10 ml 5% NaOH aq. The mixture was made slightly acidic with conc HCl, and the acidified soln was extracted with ether (5 × 4 ml). Evaporation of the ether left no residue. The water soln was made slightly more acidic with HCl and was evaporated to dryness, leaving a white solid residue. Sublimation at 150°, 0·1 mm, afforded 186 mg (1·03 mmole, 57·2%) of white crystals, mp 273–275°, IR spectrum identical with that of an authentic sample of **11**.

Reaction of bromo-lactone **4** *with* 5% *aqueous sodium hydroxide*

Bromo-lactone **4** (600 mg, 1·66 mmole) was heated at a reflux for 4 hr with 10 mg 5% NaOH aq. After acidification with conc HCl, the soln was permitted to evaporate to dryness. Sublimation of the resulting solid at 150–170°, 0·2 mm, gave 175 mg (0·94 mmole, 56·6%) of white crystals, mp 272–274°; IR identical with that of an authentic sample of **11**.

Reaction of iodolactone **5** *with sodium hydroxide*

A. *With one equivalent of sodium hydroxide.* Iodo-lactone **5** (500 mg, 1·22 mmole) was heated under reflux for 15 min with NaOH (49 mg; 1·22 mmole) in 25 ml 60% aqueous EtOH. None of the compound had dissolved by that time, so 10 ml dioxane was added to the hot soln, whereupon an immediate orange color appeared, but quickly faded, and within 5 min all of the solid had dissolved. The soln was heated for a total of 2·5 hr and, after cooling, the colorless soln was acidified with HCl and evaporated to dryness. The residue was leached with 35 ml hot $CHCl_3$. The $CHCl_3$ soln was filtered and washed successively with Na_2SO_3 aq (2 × 5 ml) and water (1 × 10 ml), and dried over $MgSO_4$. Evaporation of the $CHCl_3$ left an oily residue which, when taken up into ether and filtered, gave **11** (66 mg; 0·37 mmole, 30·3% based on lactone) as bronze plates, mp 271–273·5°; IR identical with that of an authentic sample

B. *With two equivalents of sodium hydroxide.* Iodo-lactone **5** (500 mg, 1·22 mmole) was heated under reflux for 2·5 hr with NaOH (98 mg; 2·44 mmole) in 35 ml of a 2:1:1 mixture of ethanol-water-dioxane, The pH of the resulting soln was about 6–7 (pHydrion paper). A few drops of conc HCl were added, lowering the pH to *ca* 2, and the soln was permitted to evaporate to dryness. The residue was leached with ether (4 × 20 ml). The ether soln was washed with 5 ml Na_2SO_3 aq which removed the orange color, dried over $MgSO_4$, and evaporated to give only a minute amount of an oily residue. The solid remaining after leaching with ether was sublimed at 145–170°, 0·2 mm, to give 140 mg (0·78 mmole, 63·9%) of white crystals; IR spectrum identical with that of an authentic sample of lactone **11**. TLC failed to reveal any other components in the sublimation residue.

C. *With* 5% *aqueous sodium hydroxide.* Iodo-lactone **5** (1·00 g, 2·4 mmole) was heated under reflux for

2·5 hr with 30 ml 5% NaOH aq. The orange soln was acidified with HCl and continuously extracted with ether for 2 days. The orange color in the ether extracts was removed by washing with 5% Na_2SO_3 aq. The ether layer was dried over $MgSO_4$ and evaporated to dryness to give 420 mg pink solid. Recrystallization of the solid from 1:1 ether–benzene gave 271 mg (1·5 mmole, 62·5%) of a carboxylic acid which was converted by sublimination to an anhydride, mp 165–166° (sealed tube); IR and NMR spectra identical with those of a commercial sample of **16** (Eastman Organic Chemicals, mp 164–166°).

Reaction of iodo-lactone **5** *with sodium iodide in acetone*

Iodo-lactone **5** (1·334 g, 3·26 mmole) was heated under reflux for 43 hr with 977 mg (6·52 mmole) of anhyd NaI in 50 ml dry acetone. The acetone was allowed to evaporate and the red solid residue was taken up into 100 ml ether. The ether was washed with sat Na_2SO_3 aq, water (1 × 25 ml), and dried over $MgSO_4$. Evaporation of the ether gave 1·072 g of tan solid. Fractional sublimation of the solid at 80–85°, 0·5 mm, gave, as the first fraction, 57·9 mg (0·35 mmole. 10·8% of anhydride **16** and, as the second fraction 104 mg (0·37 mmole, 11·3%) of lactol **1**. The residue (910 mg, 68·2%) was shown by IR spectral comparison to be starting material **5**.

When iodo-lactone **5** was heated under reflux for 47 hr in acetone in the absence of NaI, starting material was recovered quantitatively.

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