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THE CHEMISTRY OF PENTAVALENT ORGANOBISMUTH REAGENTS. Part IX[*]. CLEAVAGE REACTIONS OF α-GLYCOLS[†]

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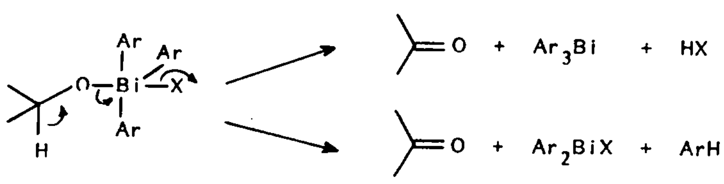
Abstract — A catalytic bismuth system (Ph_3Bi-NBS-K_2CO_3-CH_3CN with 1% water) for the cleavage of α-glycols is shown to have a different mechanism from the cyclic process observed with the stoichiometric Bi^V reagents previously studied. The catalytic system cleaves *cis*- and *trans*-decalin-9,10-diols at nearly the same rate, whereas the stoichiometric system does not cleave the *trans*-9,10-diol. Evidence for the insertion of triphenylbismuth into a hypobromite bond followed by fragmentation of the thus formed Bi^V intermediate has been secured.

The oxidation of alcohols by pentavalent derivatives of triarylbismuth 1 is a mild and efficient process, particularly for the selective oxidation of allylic type alcohols.[1,2] The reaction proceeds through a covalent Bi-O intermediate 2, which decomposes into the carbonyl derivative and triarylbismuth 3. The yield of triarylbismuth is always lower than the yield of carbonyl compound. The fragmentation of the Bi-O intermediate can follow two routes in the reductive elimination step, leading[1] either to triarylbismuth or to diarylbismuth derivative 4 with ArH acting as a leaving group (Scheme 1).



Scheme 1

Oxidation of 1,2-glycols with triphenylbismuth carbonate 5 is entirely different. 1,2-Glycols are cleaved into the corresponding carbonyl derivatives and triphenylbismuth is recovered in quantitative yield, in all cases. In this reaction, a cyclic organobismuth intermediate 6 was postulated to breaks down with exclusive formation of triphenylbismuth.[1]

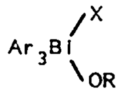
[*] Part VIII. *J. Chem. Soc. Perkin Trans. I*, in press.

[†] This paper is dedicated with affection and admiration to Professor Gilbert Stork on the occasion of his 65th birthday.

A catalytic cycle was conceptually possible. Preliminary studies indicated that cleavage of hydrobenzoin by hydrogen peroxide in the presence of sodium hydrogencarbonate, or by *t*-butylhydroperoxide, is catalysed by triphenylbismuth. The use of this system was however restricted to hydrobenzoin. But the use of *N*-bromosuccinimide (or *N*-bromoacetamide) as the oxidant of triphenylbismuth (0.01 to 0.1 equiv.) in the presence of potassium carbonate in a mixture acetonitrile-water (99:1) gave consistently good yields of carbonyl derivatives for a range of 1,2-glycols.[3]

Ar_3BiX_2

1



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Ar_3Bi

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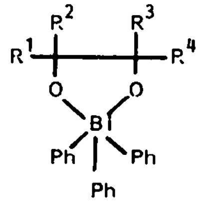


Ar_2BiX

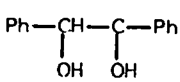
4

Ph_3BiCO_3

5

6

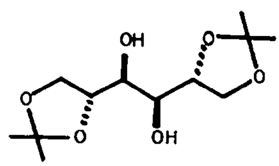
Although the described reactions were performed on a small scale (4 mmoles), the method can be applied efficiently on preparatively useful quantities of substrate. *Meso*-hydrobenzoin 7 (25 mmol) gave benzaldehyde 8 (71%). 1,2:5,6-Di-*O*-isopropylidene-D-mannitol 9 (20 mmol) gave 2,3-*O*-isopropylidene-D-glyceraldehyde 10 [52%, $[\alpha]_D$ +57.2°, (c 0.99, benzene), lit.[4] $[\alpha]_D$ +64.9° (c 1.28, benzene)]. When the aldehyde was reduced *in situ*, 2,3-*O*-isopropylidene-D-glycerol 11 was obtained [78% from 9, $[\alpha]_D$ +13.2° (c 4.56, $CHCl_3$), lit.[5] $[\alpha]_D$ +13.6° (benzene)]. These results compare favorably with the lead tetraacetate cleavage of 9.[5,6]



7

PhCHO

8



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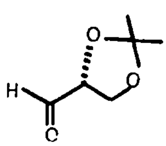
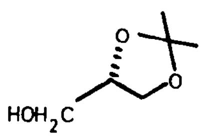


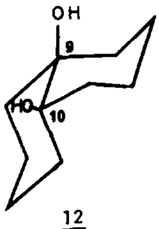
(R)-10



11

The cyclic intermediate 6 proposed for the stoichiometric oxidative cleavage of glycols with Ph_3BiCO_3 5 accounts for the smooth oxidation of *cis*-cyclohexane-1,2-diol to adipicaldehyde and for the slower cleavage of the *trans*-isomer.[1] Comparable figures were obtained for lead tetraacetate and phenyliodine(III) diacetate with a *cis:trans* relative rate of 22.9 for the lead tetraacetate cleavage.[7]

In contrast, the catalytic reaction with NBS-Ph_3Bi cleaves the *cis*-decalin-9,10-diol 12 and *trans*-isomer 13 at comparable rates. Using 0.1 equiv. of Ph_3Bi, 12 was cleaved in 2.5 hours to give 14 (72%) whilst 13 gave 14 (77%) in 3.7 hours. In the case of diols 12 and 13, the relative rate *cis:trans* for lead tetraacetate cleavage was 100,[8] and the *trans*-diol 13 failed to react at all with periodic acid.[9]



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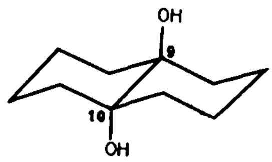

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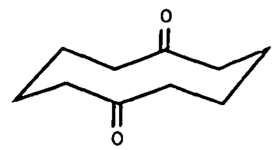

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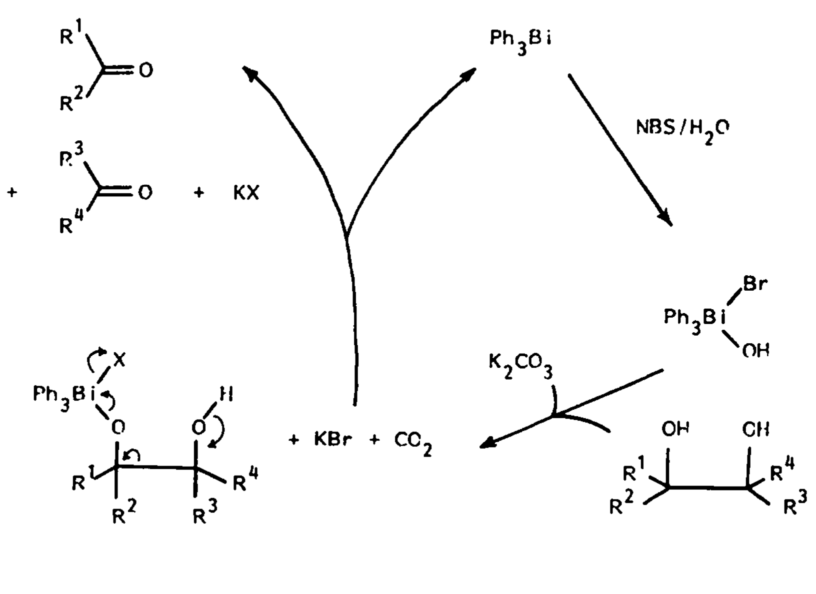
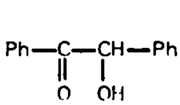
We considered therefore that the reaction could possibly be explained by the mechanism depicted in Scheme 2: i) initial formation of a pentavalent organobismuth derivative, by oxidation of Ph_3Bi to $Ph_3BiBrOH$, followed by reaction with K_2CO_3, ii) formation of a second intermediate, an alcoxytriphenylbismuth carbonate salt and iii) reductive elimination to triphenylbismuth and the carbonyl derivatives. This mechanism, as originally proposed,[3] invokes an intermediate similar to the one involved in the lead tetraacetate cleavage of *trans*-decalin-9,10-diol[10] and in the base-induced cleavage of *trans*-cyclopentan-1,2-diol by lead tetraacetate.[10,11] We decided to study the influence of the components of the reaction to elucidate its mechanism.



Scheme 2

Triphenylbismuth plays an essential role in the reaction. *N*-bromosuccinimide alone does not cleave *meso*-hydrobenzoin 7 to benzaldehyde, but oxidises it to benzoin 15 [90% with 2 equiv. of NBS]. Interestingly, *N*-iodosuccinimide, alone, effects the cleavage of 7.[12] When the reaction of NBS, 7 and K_2CO_3 was performed in the absence of Ph_3Bi and water, the oxidation did not go to completion, even after 18 hours, benzaldehyde (39%) and benzoin (7%) being obtained under these conditions. Addition of water did not improve the result : the reaction was still incomplete after 18 hours, and gave benzaldehyde (25%), benzoin (17%) and unreacted 7 (30%). Similarly, reaction with *trans*-decalin-9,10-diol 13 gave only 16% of the dione 14, after 18 hours. These results are in sharp contrast with the reaction times of the catalytic process (Table 1), and prove the necessity of Ph_3Bi. As Ph_3Bi can be expected to be oxidised to a pentavalent species, various pentavalent organobismuth compounds were reacted with 1,2-glycols (Table 2). Comparison of their efficiency towards *meso*-hydrobenzoin 7, *cis*-decalin-9,10-diol 12 and benzopinacol 16 with the catalytic system did not show any significant differences, although triphenylbismuth carbonate was less efficient, because of its poor solubility. *Trans*-decalin-9,10-diol 13 has played an important role in discussions on the mechanism of glycol fission. Kinetic comparisons of the reaction of 13 with pentavalent organobismuth compounds gave strikingly different results from the catalytic system. In the reaction of NBS on Ph_3Bi under the catalytic system conditions, various organobismuth species could be expected, among them triphenylbismuth oxide 18 and bis-succinimidotriphenylbismuth 19, which we synthesised. Whatever the conditions used (solvent, mode of addition of the reagents, presence of succinimide, of water or base) all attempts to cleave the *trans*-diol 13 with pentavalent organobismuth reagents (5, 18, 19, or Ph_3BiCl_2 20 and base) were negative. This result excluded the intermediacy of a pentavalent bismuth compound reacting with the glycol 13 to give intermediates of type 21. This closely parallels the behaviour of periodic acid which also failed to cleave 13[9] : the major pathway, if not the only one, for 1,2-glycol cleavage with stoichiometric Ph_3BiCO_3 therefore involves a cyclic intermediate, but the catalytic system is different.



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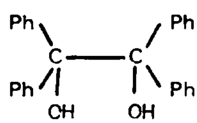

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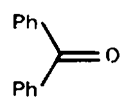

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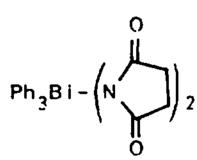
Ph_3BiO

18



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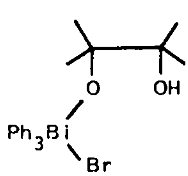
Ph_3BiCl_2

20



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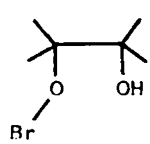

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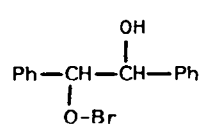

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Table 1. Catalytic α-Glycol Cleavage with Ph_3Bi-NBS-K_2CO_3 at Room Temperature.

Glycol	mMol	Ph_3Bi (equiv.)	Reaction Time (mns)	Product	Yield (%)
7	0.5	0.1	10	8	76[a]
7	5	0.1	25	8	80[a]
7	25	0.01	135	8	71
9	20	0.01	360	10	52
9	2	0.1	75	11[b]	80
9	20	0.1	360	11[b]	76
12	0.5	0.1	180	14	68
13	1.5	0.1	180	14	71
13	1.5	0.01	465	14	61
16	0.5	0.1	120	17	100

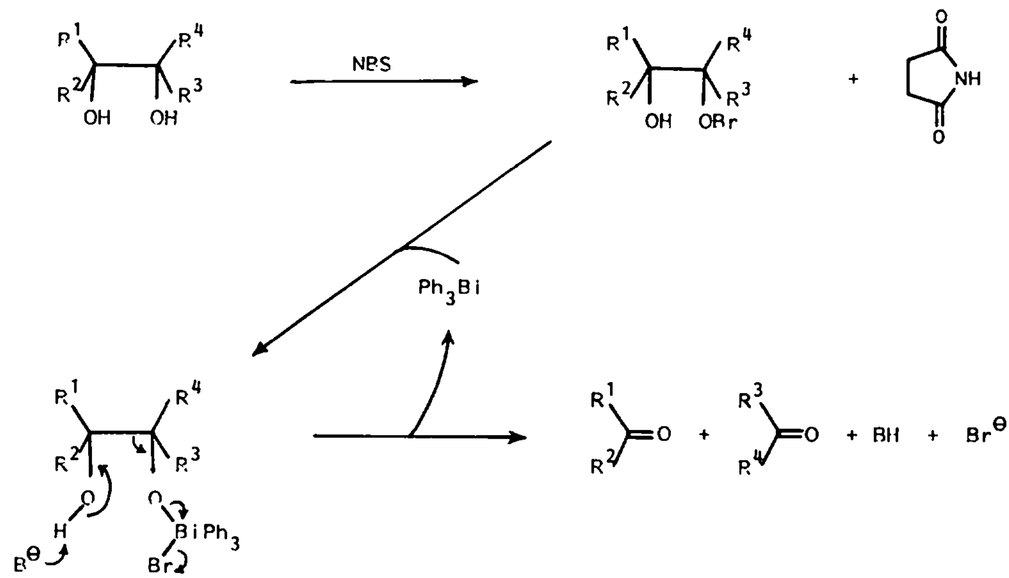
a) Isolated as the 2,4-DNP derivative. b) After *in situ* reduction of 10 with $NaBH_4$.

Table 2. Relative Reactivity of 5, 20, and the Catalytic System towards 1,2-Glycols

Glycol	Bi reagent[a]	Temperature[b]	Base	Reaction Time (hr)	Product Yield (%)
7	A	40°	-	1.5	8[b] (97)
7	B	r.t.	BTMG	0.2	8[b] (75)
7	C	r.t.	K_2CO_3	0.2	8[b] (76)
12	A	60°	BTMG	48	14 (50)
12	B	r.t.	BTMG	3	14 (71)
12	C	r.t.	K_2CO_3	2.7	14 (72)
13	A	60°	BTMG	48	14 (0)
13	B	r.t.	BTMG	3	14 (6)
13	C	r.t.	K_2CO_3	3.7	14 (77)
16	A	r.t.	-	100	17 (69)
16	B	r.t.	BTMG	1.5	17 (77)
16	C	r.t.	K_2CO_3	2	17 (100)
16	D	r.t.	K_2CO_3	1.5	17 (84)

a) A: Ph_3BiCO_3, B: Ph_3BiCl_2, C: NBS + Ph_3Bi (0.1 equiv.), D: NBS + Ph_3Bi (0.01 equiv.)
b) r.t.: room temperature. c) Isolated as the 2,4-DNP derivative.

An alternative mechanism, as depicted in Scheme 3, could then explain the catalytic reaction. Oxidation of alcohols with *N*-bromosuccinimide and *N*-bromoacetamide have been postulated to occur through a hypobromite.[12,13,14] In the reaction with glycols, such an intermediate 22 could act as the oxidant of triphenylbismuth to give the second intermediate 21. Reductive elimination would yield the reaction products.



Scheme 3

In the first step, *N*-bromosuccinimide oxidises the glycol to a glycol monohypobromite and succinimide. Monitoring of the reaction by ^{1}H-NMR clearly revealed the presence of two singlets (δ 2.85 ppm for NBS and 2.65 ppm for succinimide). Reaction of NBS and K_2CO_3 with hydrobenzoin gave succinimide (90% after only 5 mins.). In the catalytic reaction with *trans*-decalin-9,10-diol 13, succinimide was also isolated (80%). Moreover, in the reaction of NBS with 7, when the precipitate of succinimide was filtered, and K_2CO_3 and Ph_3Bi added to the solution, benzaldehyde (45%) was obtained.

Isolation of the pure glycolhypobromite was not possible. Nevertheless, detection of its presence was attempted by spectroscopy. Addition of NBS to a $CDCl_3$ solution of hydrobenzoin induces a downfield shift for one of the two -CHOH- (δ 5.9 instead of 4.7 ppm).

Hydrogen bromide catalyses the reaction in $CHCl_3$. Formation of succinimide was complete in only 5 mins. after addition of 0.4 equiv. of HBr to a $CDCl_3$ solution of 7 and NBS. Under these conditions, the oxidant is bromine. When the reaction is performed in acetonitrile, K_2CO_3 also acts as a catalyst for the reaction of NBS and the glycol 7. When the evolution of a mixture of 7 and NBS in d_3-acetonitrile was monitored by ^{1}H-NMR, only 30% of succinimide was formed after 5 mins. Addition of D_2O did not change the ratio, but after addition of K_2CO_3, the NBS signal quickly disappeared.

The course of the reaction between the glycol and NBS being completely modified by addition of Ph_3Bi, we tried, but without success, to detect a covalent Bi-O intermediate. However, triphenylarsenic and triphenylantimony are known to react with *t*-butylhypohalite to give isolable alcoxyhalo derivatives,[15] but such a reaction with triphenylbismuth is not known.

The role of the base is also important. It can either act as a trap for any acid formed or catalyse the cleavage of the intermediate. When propylene oxide was used instead of K_2CO_3 as a trap for HBr, no cleavage product was detected even after 18 hours.

Another important element of the catalytic reaction is water. It can either catalyse the formation of a hypobromite species or solubilise K_2CO_3. The use of organic bases appeared to be detrimental to the reaction.[3] Diethylamine, *N,N*-dimethylaniline and triethylamine prevented the catalytic reaction. Similarly pyridine was inefficient : hydrobenzoin, NBS and pyridine gave only benzoin after 20 hours, in a low yield (29%).

These mechanistic studies on the α-glycol cleavage with pentavalent organobismuth compounds have proven the occurence of two different pathways. The stoichiometric α-glycol cleavage with triphenylbismuth carbonate goes through a cyclic covalent intermediate and hence is closely related to the periodic acid α-glycol cleavage, known to involve only one pathway. In the catalytic α-glycol cleavage by the NBS-Ph_3Bi-K_2CO_3 system, no cyclic intermediate is formed. In the first step, the glycol reacts with NBS to form a hypobromite, which itself acts as an oxidant of Ph_3Bi to form a pentavalent alcoxy intermediate such as 21. The last step is the base-induced reductive elimination with cleavage of the (O)-C-C-(O) bond to the carbonyl derivatives and triphenylbismuth. When possible, the intermediacy of a cyclic bismuth dialcoxyde cannot be excluded as a minor pathway of the catalytic reaction.

Experimental

M.p.'s were determined with a Kofler hot-stage apparatus and are uncorrected. N.m.r. spectra were determined for solutions in deuteriochloroform with $SiMe_4$ as an internal standard on Varian T-60, Varian E-M 360 or Bruker WP-80 instruments. I.r. spectra were recorded on a Perkin-Elmer 297 apparatus. Optical rotations were measured on a Perkin-Elmer 141-MC polarimeter. Mass spectra were recorded with an AEI MS-9 or MS-50 instrument. All solvents and reagents were purified and dried by standard techniques. Chromatographic separations were performed using Merck Kiesegel 60 GF 254 (preparative t.l.c.) and Merck Kieselgel 60-H (column chromatography). Aqueous acetonitrile refers to a solution of H_2O (1%) in acetonitrile, and ether refers to diethylether. BTMG is *N*-*t*-butyl-*N'*,*N'*,*N"*,*N"*-tetramethylguanidine.

Cleavage of 1,2-Glycols : General Method

A solution of *N*-bromosuccinimide (1.1 to 1.5 equiv.) in aqueous acetonitrile (10 ml per mMole of NBS) was added dropwise over a period of time indicated (t_1) to a mixture of glycol (1 equiv.), triphenylbismuth (0.01 to 0.1 equiv.) and K_2CO_3 (10 equiv.) in aqueous acetonitrile (10 ml per mMole of glycol), in the dark at room temperature. The mixture was then stirred for a further period (t_2). After filtration, the solvent was distilled under vacuum. The residue was extracted with a mixture water-ether. The organic phase was dried over Na_2SO_4, the solvent distilled under vacuum, and the residue purified by preparative t.l.c.

a) Hydrobenzoin 7 (0.5 mMol) and Ph_3Bi (0.1 equiv.).- 7 (0.107 g), NBS (0.098 g), Ph_3Bi (0.022 g) and K_2CO_3 (0.690 g) in t_1 5 minutes and t_2 5 minutes gave benzaldehyde 8 as the 2,4 DNP derivative (0.216 g, 76%).

b) 7 (5 mMol) and Ph_3Bi (0.1 equiv.).- 7 (1.07 g), NBS (0.98 g), Ph_3Bi (0.22 g) and K_2CO_3 (6.9 g) in t_1 10 minutes and t_2 15 minutes gave the 2,4-DNP of 8 (2.28 g, 80%).

c) 7 (25 mMole) and Ph_3Bi (0.01 equiv.).- 7 (5.35 g), NBS (4.90 g), Ph_3Bi (0.110 g) and K_2CO_3 (38 g) in t_1 1 hour and t_2 1.25 hours gave 8 after distillation (3.76 g, 71%).

d) 1,2:5,6-Di-*O*-isopropylidene-D-mannitol 9 (20 mMol) and Ph_3Bi (0.01 equiv.).- 9 (5.2 g), NBS (3.8 g), Ph_3Bi (0.088 g) and K_2CO_3 (27.6 g) in t_1 4 hours and t_2 2 hours gave 10 (2.6 g, 52%), as an oil, $[\alpha]_D$ +57.2° (c 0.99, benzene), lit.[4] +64.9° (benzene).

e) 9 (2 mMol), Ph_3Bi (0.1 equiv.), followed by $NaBH_4$ reduction to 11.- To the reaction of 9 (0.52 g), NBS (0.376 g), Ph_3Bi (0.088 g) and K_2CO_3 (2.7 g) in t_1 0.5 hour and t_2 0.75 hour was added $NaBH_4$ (0.076 g) in methanol (10 ml). The mixture was stirred at 40°C for 4 hours. The solvents were distilled under vacuum at room temperature. The residue was dissolved in saturated aqueous ammonium chloride (60 ml) and brine (150 ml). The solution was extracted with ether (6x30 ml), then by continuous extraction overnight with ether (100 ml). The organic phases were distilled under vacuum and the residue purified by column chromatography [eluant: hexane-ether 4:1 (200 ml) followed by ether (300 ml)] to yield 11 (0.426 g, 80%), as an oil, $[\alpha]_D$ +11.1° (c 2.46, $CHCl_3$), lit.[5] +13.6 (benzene); ν_{max} (CH_2Cl_2): 3500, 2900, 1390, and 1210 cm^{-1}; δ ($CDCl_3$): 4.1-3.4 (5H, m, CH_2 and CH), 2.1 (1H, m, OH), and 1.35 and 1.3 (6H, 2s, $2xCH_3$).

f) 9 (20 mMol) and Ph_3Bi (0.1 equiv.) followed by $NaBH_4$ reduction to 11.- The reaction of 9 (5.2 g), NBS (3.8 g), Ph_3Bi (0.88 g) and K_2CO_3 (27 g) in t_1 4 hours and t_2 6 hours was treated with a solution of $NaBH_4$ (0.76 g) in methanol (100 ml). Work-up as in experiment e) gave 11 (3.96 g, 76%), $[\alpha]_D$ + 13.2° (c 4.56, $CHCl_3$), which on treatment with p-nitrobenzoylchloride in pyridine for 20 hours at room temperature yielded a crystalline derivative (83%), m.p. 43-45°C (ether), lit.[16] 36.5-37°; $[\alpha]_D$ +6.4° (c 2.34, pyridine), lit.[16] +5.8° (pyridine) [Found: C, 55.59; H, 5.30; N, 5.27; O, 34.23. Calc. for $C_{13}H_{15}NO_6$: C, 55.52; H, 5.34; N, 4.98; O, 34.16%].

g) 12 (0.5 mMole) and Ph_3Bi (0.1 equiv.).- 12 (0.085 g), NBS (0.130 g), Ph_3Bi (0.022 g) and K_2CO_3 (0.690 g) in t_1 130 minutes and t_2 50 minutes gave 14 (0.057 g, 68%), m.p. 96-98°C (ether), lit.[3,17] 98-99°C; m/z 168 (M^+).

h) 13 (1 mMole) and Ph_3Bi (0.1 equiv.).- 13 (0.170 g), NBS (0.261 g), Ph_3Bi (0.044 g) and K_2CO_3 (1.38 g) in t_1 160 minutes and t_2 20 minutes gave 14 (0.120 g, 71%).

i) 13 (1 mMole) and Ph_3Bi (0.01 equiv.).- 13 (0.170 g), NBS (0.261 g), Ph_3Bi (0.004 g) and K_2CO_3 (1.38 g) in t_1 6 hours and t_2 1.75 hours gave 14 (0.102 g, 61%).

j) 16 (0.5 mMole) and Ph_3Bi (0.1 equiv.).- 16 (0.183 g), NBS (0.098 g), Ph_3Bi (0.022 g) and K_2CO_3 (0.690 g) in t_1 1 hour and t_2 1 hour gave 17 (0.182 g, 100%).

Oxidation of Hydrobenzoin 7 and *trans*-Decalin-9,10-diol 13

a) Reaction of NBS and 7.- A solution of 7 (0.107 g) and NBS (0.178 g) in anhydrous acetonitrile (10 ml) was stirred at room temperature for 10 hours. After filtration, the solvent was distilled off under vacuum. The residue was extracted with a mixture water-ether. Preparative t.l.c. of the ether soluble residue afforded benzoin 15 (0.095 g,90%).

b) In the presence of K_2CO_3.- A similar reaction performed in the presence of K_2CO_3 (0.690 g) gave after 18 hours 8 (0.041 g, 39%), 15 (0.007 g, 7%), and 7 (0.015 g, 14%).

c) In the presence of K_2CO_3 and H_2O.- When experiment b) was performed in aqueous acetonitrile for 18 hours, 8 (0.041 g, 39%), 15 (0.009 g, 8%), and 7 (0.032 g, 30%) were formed.

d) With dropwise addition of NBS.- A solution of NBS (0.178 g) in aqueous acetonitrile (5 ml) was added drowpise over 3 hours to a mixture of 7 (0.107 g) and K_2CO_3 (0.690 g) in aqueous acetonitrile (5 ml), at room temperature in the dark. The mixture was stirred for a further 18 hours. Work-up afforded 8 (0.026 g, 25%), 15 (0.018 g, 17%), and 7 (0.031 g, 29%).

e) Reaction of NBS and 13.- A solution of NBS (0.430 g) in aqueous acetonitrile (5 ml) was added dropwise over 3 hours to a mixture of 13 (0.085 g) and K_2CO_3 (0.690 g) in aqueous acetonitrile (3 ml), at room temperature in the dark. The mixture was stirred for a further 18 hours. Work-up afforded 14 (0.013 g,10%), and 13 (0.065 g, 76%).

Cleavage of 1,2-Glycols with Triphenylbismuth Carbonate 5

a) A mixture of *cis*-decalin-9,10-diol 12 (0.085 g), 5 (0.375 g) and BTMG (0.19 ml) in THF (5 ml) was stirred under reflux for 2 days to give, after work-up, 14 (0.043 g, 50%), and 12 (0.025 g, 30%).

b) A mixture of *trans*-decalin-9,10-diol 13 (0.085 g), 5 (0.375 g) and BTMG (0.19 ml) in THF (5 ml) under reflux for 2 days gave 13 (0.080 g, 94%) after work-up.

c) A mixture of benzopinacol 16 (0.183 g) and 5 (0.375 g) in THF (5 ml) was stirred at room temperature for 4 days. After filtration and distillation under vacuum, preparative t.l.c. of the residue (eluant: ether-hexane 1:4) afforded 17 (0.125 g, 69%).

d) A mixture of 16 (0.183 g), 5 (0.375 g) and K_2CO_3 (0.690 g) in aqueous acetonitrile (10 ml) after 11 hours at room temperature gave 17 (0.138 g, 76%).

e) A mixture of 16 (0.183 g), 5 (0.375 g) and BTMG (0.14 ml) in THF (5 ml) after 9 hours at room temperature gave 17 (0.144 g, 79%).

Cleavage of 1,2-Glycols with Triphenylbismuth Dichloride 20

a) A solution of 7 (0.065 g), 20 (0.205 g) and BTMG (0.125 ml) in CH_2Cl_2 (3 ml) was stirred at room temperature for 10 minutes. After addition of a solution of 2,4-DNP in methanol, the 2,4-DNP derivative of 8 was obtained (0.128 g, 75%).

b) A solution of 12 (0.085 g), 20 (0.335 g) and BTMG (0.22 ml) in CH_2Cl_2 (5 ml) was stirred at room temperature for 3 hours. Work-up and preparative t.l.c. afforded 14 (0.060 g, 71%).

c) A solution of 13 (0.085 g), 20 (0.335 g) and BTMG (0.22 ml) in CH_2Cl_2 (5 ml) was stirred at room temperature for 3 hours. Work-up and preparative t.l.c. afforded 14 (0.005 g, 6%) and 13 (0.076 g, 88%).

d) A solution of 16 (0.110 g), 20 (0.205 g) and BTMG (0.125 ml) in CH_2Cl_2 (3 ml) was stirred at room temperature for 90 minutes. Work-up and preparative t.l.c. afforded 17 (0.084 g, 77%).

Formation of a Hypobromite Intermediate

NMR study of the cleavage of 7.- A solution of NBS (0.018 g) in deuterated acetonitrile (0.5 ml) and D_2O (0.005 ml) was added over 5 minutes to a mixture of 7 (0.021 g) and K_2CO_3 (0.138 g) in D_2O (0.005 ml) and CD_3CN (0.5 ml). The reaction evolution was monitored by ^1H NMR. At t = 0, δ (ppm) 7.05 (10H, s, ArH), 4.7 (2H, s, CH), 2.7 (4H, s, CH_2 of NBS), and 2.25 (2H, s, OH). The NBS signal quickly disappeared, and a signal (succinimide) appeared at 2.6 ppm with a similar intensity. Triphenylbismuth (0.004 g) was added. After 5 minutes, the NMR spectrum showed : δ 9.9 (1H, s, CHO), 7.85-7.25 (5H, m, ArH), and 2.6 (4H, s, CH_2 of succinimide). The ratio of the integrations gave a 71% yield of benzaldehyde. After filtration of the mixture, the solvent was distilled at room temperature under reduced pressure. The residue was dissolved in ether, washed with water and a methanolic solution of 2,4-DNP added. The DNP derivative of benzaldehyde was isolated (0.014 g, 50%).

Isolation of Succinimide during the Catalytic Cleavage of 7. A mixture of 7 (0.107 g), NBS (0.098 g) and K_2CO_3 (0.690 g) in aqueous acetonitrile (5 ml) was stirred at room temperature in the dark for 5 minutes. The solvent was then distilled under vacuum in the dark. After addition of CCl_4, the mixture was filtered. The precipitate was washed with acetonitrile to yield succinimide (0.045 g, 90%). The solution was distilled under vacuum and the residue dissolved in aqueous acetonitrile (5 ml). Triphenylbismuth (0.022 g) and K_2CO_3 (0.690 g) was added and the mixture stirred for 5 minutes at room temperature in the dark. Work-up and treatment with 2,4-DNP as above afforded the 2,4-DNP derivative of 8 (0.064 g, 45%).

Isolation of Succinimide during the Catalytic Cleavage of 13.- A mixture of 13 (0.034 g), NBS (0.036 g) and K_2CO_3 (0.276 g) in d_3-acetonitrile (1 ml) containing D_2O (1%) was stirred at room temperature in the dark. The reaction was monitored by ^1H-NMR. After complete disappearance of the NBS signal (δ 2.85 ppm), the mixture was added dropwise over 2.5 hours to a mixture of Ph_3Bi (0.009 g) and K_2CO_3 (0.276 g) in aqueous acetonitrile (1 ml). The mixture was stirred for a further 5.3 hours. After filtration, the solvent was distilled off under reduced pressure, and preparative t.l.c. of the residue afforded 14 (0.016 g, 45%) and succinimide (0.016 g, 80%).

NMR Study of the Influence of Water and Potassium Carbonate on the Formation of Succinimide.- The evolution of a solution of 7 (0.011 g), NBS (0.010 g) in CD_3CN (1 ml) kept in the dark at room temperature was followed by NMR. After 5 minutes, the ratio (δ 2.85):(δ 2.65) was 7:3. No modification occurred after addition of D_2O (10 μl). The δ 2.85 signal completely disappeared after addition of K_2CO_3 (0.069 g). The spectrum showed : δ 8-7.1 (10H, m, Ar-H), 5.9 (1H, m, CH-OBr), 4.7 (1H, m, CH-OH), and 2.35 (1H, m, OH). Triphenylbismuth (0.022 g) was added. The signals at δ 5.9 and 4.7 disappeared while a signal δ 10 appeared (1H, s, CHO). In a blank experiment, NBS was stable in a solution of CD_3CN-D_2O, but converted to succinimide upon addition of K_2CO_3.

Acid Catalysis.- Hydrobromic acid (0.2 to 1 equiv.) was added to a solution of 7 (0.013 g) and NBS (0.010 g) in $CDCl_3$ (0.5 ml). The evolution of the reaction was followed by ^1H-NMR. With 0.2 equiv. of HBr, the amount of succinimide was : t = 5 min., 70%; t = 15 min., 92%; t = 30 min., 100%. With 0.3 equiv. : t = 5 min., 80%; t = 15 min., 100%. With 0.4 equiv.: t = 5 min., 100%.

Reduction of the Hypobromite.- A solution of 7 (0.107 g) and NBS (0.089 g) in $CHCl_3$ (5 ml) was stirred in the dark at room temperature, until the signal of NBS had disappeared in the NMR spectrum. A solution of sodium bisulphite in methanol-water (1:1) was added and the mixture stirred for 1 hour. Work-up afforded 7 (0.073 g, 68%) and 15 (0.032 g, 30%).

Attempted Catalytic Cleavage with Pyridine as Base

A solution of 7 (0.043 g), NBS (0.039 g) and HBr (6 μl) in $CDCl_3$ was stirred in the dark at room temperature for 5 minutes. Ph_3Bi (0.009 g) and pyridine (49 μl) in $CHCl_3$ (1 ml) was added. The reaction was stirred overnight in the dark at room temperature. Usual work-up afforded 15 (0.012 g, 29%) and 7 (0.024 g, 57%).

Reaction in the Presence of Propylene Oxide

a) In absence of base.- A solution of 7 (0.041 g) and NBS (0.039 g) in $CDCl_3$ (2 ml) was stirred in the dark at room temperature. After disappearance of the NBS signal, propylene oxide (0.024 g) was added. No modification had occurred in the NMR spectrum after 30 minutes. Ph_3Bi (0.009 g) was added and the mixture stirred for 18 hours. Benzaldehyde was not detected. Work-up afforded 7 (0.017 g, 41%) and 15 (0.023 g, 55%).

b) With BTMG.- A solution of 7 (0.041 g), NBS (0.039 g) and HBr (8 μl) in $CDCl_3$ (2 ml) was stirred in the dark at room temperature until NBS was consumed. Propylene oxide (0.024 g) was added. No evolution was noted after 30 minutes. Ph_3Bi (0.009 g) and BTMG (0.038 g) in

$CDCl_3$ (0.5 ml) were added. The signal at δ 4.8 ppm disappeared to give a ratio 8:15 equal to 9:1 as determined by the integration of the signals at δ 9.85 (PhCHO) and 5.9 (Ph-CHOH-CO-Ph) ppm. After distillation under vacuum, the residue was extracted in a mixture ether-water. Addition of 2,4-DNP reagent to the ethereal phase, followed by column chromatography of the DNP derivatives afforded the DNP of 8 (0.097 g, 85%) and the DNP of 15 (0.009 g, 12%).

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