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GLYCOL-CLEAVAGE REAGENTS ALSO ACT ON STANNYLENE DERIVATIVES.

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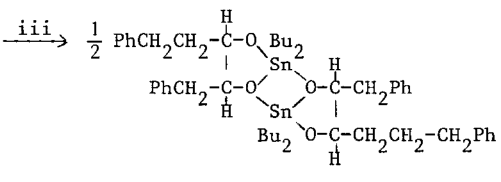
The well-known cleavage reactions of vicinal diols by such reagents as $Pb(OAc)_4$, $NaIO_4$, $PhI(OAc)_2$ and Ph_3Bi^V-compounds have now been observed for the first time on covalent derivatives of these vicinal diols, their dibutylstannylenes.

Dibutylstannylene derivatives, readily available from diols in quantitative yield,[1,2] exist as dimers with a general structure such as 3 (see below) in the solid state,[3] in weakly or non polar solvents,[3,4] and in the gas phase.[4] Dibutylstannylation activates regiospecifically one oxygen atom of a diol towards electrophilic attack,[5,6] while the adjacent carbon atom is easily oxidized by bromine, leading to a hydroxy-ketone.[7,8] Dibutylstannylenes are readily soluble in weakly or non polar solvents, even light petroleum, and then the ^{119}Sn n.m.r. chemical shifts of the solutes appear in the range characteristic of pentacoordinate tin.[3,4,9] Lighter representatives show relatively low boiling points. Field desorption mass spectrometry gives one, dimeric molecular peak.[4] These evidences, and the length of the Sn-O bonds in the crystal,[3] indicate that tin is covalently linked to oxygen within the 5-membered ring.

Typical glycol cleavage has been described with free glycols only, although reports of catalysis by sodium acetate[10] or strong organic bases[11] suggest that the derived alcoholates may be more reactive. We now report carbon-carbon bond cleavage of the covalent stannylene derivatives in CH_2Cl_2 with $Pb(OAc)_4$, $BuN^+IO_4^-$ (ref.[12]), $PhI(OAc)_2$ and a member of the recently introduced Ph_3Bi^V family of reagents,[11] $Ph_3Bi(OAc)_2$, chosen because of its solubility in CH_2Cl_2. Stannylene 3 was synthesized as a most general and convenient substrate for the study of typical cleavage. From the Z-olefin 1 (b.p. 146°C at 1.5 mm Hg, compatible ^1H n.m.r. spectrum),[13] the crystalline erythro diol 2 was prepared (78%; m.p. 83°C from light petroleum)[13] and converted to the stannylene 3.

Scheme.

$Ph(CH_2)_3PPh_3{}^+Br^- \xrightarrow{i}$ Z-$PhCH_2$-CH_2-CH=CH-CH_2Ph (1) $\xrightarrow{ii}$ DL-erythro-$PhCH_2$-CH_2-CHOH-CHOH-CH_2Ph (2)



(3)

i) $NaNHSiMe_3$, $PhCH_2CHO$, in the conditions of Bestmann et al.[14]; ii) N-methylmorpholine-N-oxide, OsO_4, according to [15]; iii) Bu_2SnO, azeotropic removal of water.
Results are reported in Table I (first entries).

Table I. Oxidation of stannylene 3.[a]

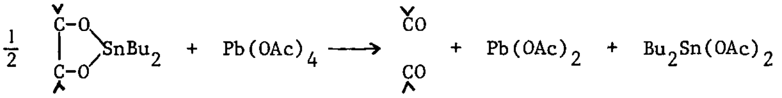
Oxidant	Equiv.	Temperature °C	Time	$PhCH_2CHO$ %	$PhCH_2CH_2CHO$ %
$Bu_4\overset{+}{N}IO_4^-$	1	RT	5 min	82	99
$Pb(OAc)_4$	1	RT	5 min	85	91
$PhI(OAc)_2$	1	RT	5 min	(b)	98
$Ph_3Bi(OAc)_2$	1.5	40	2 h	66	90
$Cr_2O_2Cl_2$	1.2	-78 → RT	3 h	11	15
$Bu_4N^+MnO_4^-$	1	RT	16 h	x	x
$Tl(OCOCF_3)_3$	1	40	2 h	x	x

[a] The oxidant was added to a solution kept under N_2 of the stannylene (0.5 mmole of the dimer) in CH_2Cl_2 (5 ml). When there was no more starting material (t.l.c.), the solution was filtered through a small column of silica gel and concentrated to a small volume. Yields were estimated by g.l.c. (SE 30, 130°C) with n-tridecane as internal standard.

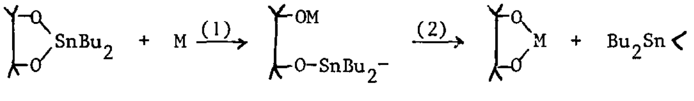
[b] Interference from PhI made the estimation impossible.

The oxidation of 0.01 M solution of 3 in CH_2Cl_2 is very fast and should be considered as quantitative, despite the low recovery of $PhCH_2CHO$ due to its volatility. The possibility to achieve glycol cleavage under strictly aprotic conditions in non polar solvents should be interesting in mechanistic studies, for rates are known to me markedly pH-dependent.[16] It may also be useful in preparative chemistry, for instance, when the evolution of acetic acid must be avoided.

Stoechiometries similar to the following one are likely :



This new reaction of stannylenes seems to be yet another consequence of their enhanced nucleophilicity : one of their oxygen atoms binds readily to the higher valency iodine, lead or bismuth atom. The cleavage of 1,2-diols is supposed to involve a two-steps ring-closure to cyclic esters. The analogous reaction of stannylenes would be such :



From what is known about stannylene chemistry, reaction (2) of the deactivated oxygen atom should be very sluggish, although in the present case it might be accelerated by a proximity effect. But a new mechanism may be operative from the beginning, for instance insertion of I=O or Pb-O-C=O groups into a Sn-O bond.

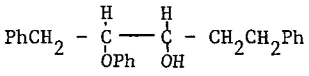
We have observed many instances of the spliting of stannylenes with the above reagents, but attempts to extend these reactions showed that stannylenes were not more general substrates than their parent diols : Reagents such as $Tl(OCOCF_3)_3$,[17] $Bu_4N^+MnO_4^-$,[18] and CrO_2Cl_2 are as ineffective (Table I, last entries). These oxidants are able to split meso-hydrobenzoin[19] (at least sometimes by another mechanism). Stannylation of meso-hydrobenzoin did not change much to the oxidation by $Tl(OCOCF_3)_3$, while the permanganate oxidation was efficiently derived towards the production of benzaldehyde (the free diol gave 39% benzile). The reverse was true with CrO_2Cl_2 (Table II).

Table II. Oxidation of the stannylene of hydrobenzoin [a]

Oxidant	Temperature °C	Time h	PhCHO % by weight	$(PhCO)_2$ % by weight
$Tl(OCOCF_3)_3$	40	0.5	66.5	10
$Bu_4N^+MnO_4^-$	RT	1	57	0
$Cr_2O_2Cl_2$	RT	5	17.5	42.5

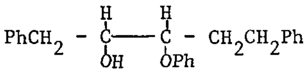
[a] Conditions were the same as for Table I, with one equivalent of oxidant. Internal CPV standards were dodecane for PhCHO (90°C) and hexadecane for benzile (200°C).

Now coming back to Table I, we see that the reaction of $Ph_3Bi(OAc)_2$ on stannylene **3** recalls the oxidation with Ph_3BiCO_3 of a free diol in the presence of a strong base.[11] On the other hand, we found that refluxing the free diol **2** for 2 h in CH_2Cl_2 in the presence of $Ph_3Bi(OAc)_2$ without added base effected a quantitative conversion to two closely related products which could be separated by capillary column gas chromatography (OV1, 200°C). The spectral properties were consistent with the presence of the phenyl ethers **4** and **5** [m.s. : m/e 332 (molecular peak), 94 (PhOH); ν_{max} 3440, 3560 cm^{-1}, no C=O absorption; δ (250 MHz, $CDCl_3$, Me_4Si) : 2.00 (1H, d, $J_{\underline{H},OH}$ 4 Hz, OH), 3.96 (1H, d, $J_{\underline{H},OH}$ 3 Hz, OH), 3.81 (1H, m, $\underline{H}$-C-OH), 4.09 (1H, m, $\underline{H}$-C-OH), 4.22 (1H, m, $\underline{H}$-C-OPh), 4.40 (1H, m, $\underline{H}$-C-OPh); for the mixture of acetates : δ 4.98 (1H, m, $\underline{H}$-C-OAc), 5.18 (1H, m, $\underline{H}$-C-OAc)].



$PhCH_2-\underset{OPh}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-CH_2CH_2Ph$

4



$PhCH_2-\underset{OH}{\overset{H}{C}}-\underset{OPh}{\overset{H}{C}}-CH_2CH_2Ph$

5

Accordingly, refluxing for 4 hours a solution of the symmetrical 1,2-*trans*-cyclohexanediol in CH_2Cl_2 in the presence of one equivalent of $Ph_3Bi(OAc)_2$ gave in 88% isolated yield *trans* 2-phenoxy-cyclohexanol,[13] m.p. 81-82°C (from ether-light petroleum), further characterized as the paratoluensulfonate, m.p. 116-117°C (from ether), and identical in every respect with the known compound.[20] Although the preparation of a phenyl ether of paranitrophenol with Ph_5Bi has been reported,[21] the reactions described here seem to involve distinct features and to be specific for diols, for cyclohexanol is unchanged on 7 hours refluxing in CH_2Cl_2 in the presence of $Ph_3Bi(OAc)_2$.

Dibutylstannylation thus alters drastically the outcome of the reaction of vicinal diols with $Ph_3Bi(OAc)_2$. With the other reagents, its effect may be probably best described in terms of rate and yields, for the aprotic conditions necessarily change the nature of some intermediates.

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