Formation of 3,6-Dialkyl-1,2,4,5-tetraoxans and Related Cyclic Bis(peroxides) by the Action of Antimony Pentachloride or Chlorosulphonic Acid on Ozonides

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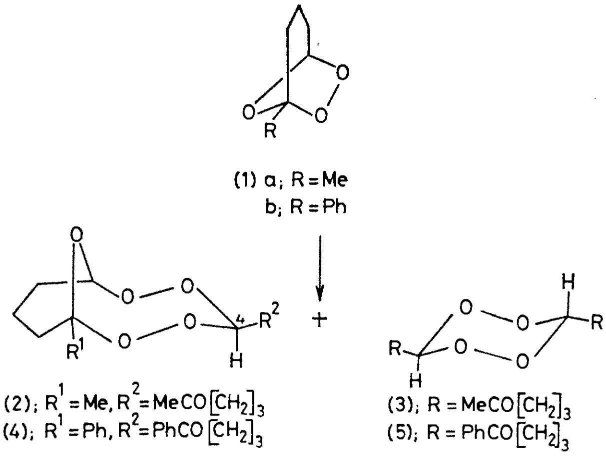
Summary The reaction of some ozonides (1,2,4-trioxolans) with catalytic amounts of $SbCl_5$ or $ClSO_3H$ in methylene chloride affords 3,6-dialkyl-1,2,4,5-tetraoxans or 1,4-dialkyl-2,3,5,6,11-pentaoxabicyclo[5.3.1]undecanes.

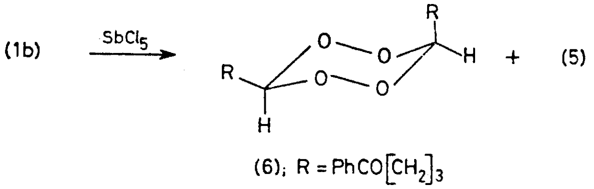
The reactions of some 1,2,4-trioxolans (ozonides) with acid catalysts have been examined, but only the rearrangement[1,2] or reduction products[3,4] have been obtained. We now report that the reaction of ozonides with catalytic amounts of $SbCl_5$ or $ClSO_3H$ affords the 3,6-dialkyl-1,2,4,5-tetraoxans and/or 1,4-dialkyl-2,3,5,6,11-pentaoxabicyclo[5.3.1]undecanes.


(1) a; R = Me
b; R = Ph

(2); R^1 = Me, R^2 = MeCO[CH_2]$_3$
(4); R^1 = Ph, R^2 = PhCO[CH_2]$_3$

(3); R = MeCO[CH_2]$_3$
(5); R = PhCO[CH_2]$_3$

To a solution of 1-methyl-6,7,8-trioxabicyclo[3.1]-2.octane (**1a**) (1 g) in methylene chloride (20 ml), was added $SbCl_5$ (0·23 mmol) in methylene chloride (20 ml) in one portion, and the mixture was left at 20 °C for 30 min. After work-up the neutral products were chromatographed on silica gel using benzene–ether (4 : 1). The first fraction contained 0·32 g (32% yield) of 1-methyl-2,3,5,6,11-pentaoxa-4-*exo*-(4-oxopentyl)bicyclo[5.3.1]undecane (**2**);† liquid, δ 1·46 (3H, s, Me), 1·48—2·04 (10H, m), 2·12 (3H, s, COMe), 2·46 (2H, t, J 6·8 Hz, $COCH_2$), 5·34 (1H, s, H-7), and 5·54 (1H, t, J 5·1 Hz, H-4); ν_{max} 1720 cm^{-1}. The second fraction contained 0·29 g (29% yield) of *trans*-3,6-bis(4-oxopentyl)-1,2,4,5-tetraoxan (**3**);† m.p. 79—80 °C, δ 1·24—1·96 (8H, m), 2·16 (6H, s, Me), 2·48 (4H, t, J 6·2 Hz, $COCH_2$), and 5·85 (2H, t, J 5·1 Hz, H-3 and H-6); ν_{max} 1715 cm^{-1}. The fact that 44% of (**2**) rearranges to (**3**) in the presence of 0·06 mol. equiv. of $SbCl_5$ within 30 min suggests that (**2**) is formed from (**1a**) almost exclusively.


(6); R = PhCO[CH_2]$_3$

The reaction of (**1a**) with 0·03 mol. equiv. of $ClSO_3H$ gave (**2**) in 45% yield with 14% of (**1a**) being recovered. Similar behaviour was observed in the reaction of the phenyl derivative (**1b**) with $ClSO_3H$. The products were

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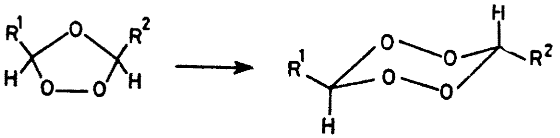
† All new compounds gave satisfactory elemental analyses. Yields were calculated on the assumption that 1 mol. of the tetraoxan is formed from 2 mol. of the ozonide. Molecular weights, measured using a vapour pressure osmometer, were consistent with calculated values.

triturated with ether, to give compound (**4**) in 55% yield;† m.p. 144—145 °C, δ 1·40—2·04 (10H, m), 2·95 (2H, t, *J* 5·7 Hz, $COCH_2$), 5·60 (1H, s, H-7), and 5·72 (1H, t, *J* 5·7 Hz, H-4); ν_{max} 1695 cm^{-1}. Column chromatography of the mother liquor on silica gel gave (**5**) in 7% yield;† m.p. 147—148 °C, δ 1·48—2·08 (8H, m), 2·98 (4H, t, *J* 6·8 Hz, $COCH_2$), and 5·88 (2H, t, *J* 5·1 Hz, H-3 and H-6); ν_{max} 1680 cm^{-1}. In contrast, the reaction of (**1b**) with $SbCl_5$ gave a mixture of the *cis*-tetraoxan (**6**) (35% yield after 30 min, 37% after 5 min)† and the *trans*-isomer (**5**) (20% yield after 30 min, 9% after 5 min). The *cis*-tetraoxan (**6**) has the following properties; m.p. 106—107 °C, δ 1·48—2·16 (8H, m), 2·98 (4H, t, *J* 6·8 Hz, $COCH_2$), 5·47 (1H, br. s, H-3, *eq.*), and 5·68 (1H, t, *J* 5·4 Hz, H-6, *ax.*); ν_{max} 1690 and 1680 cm^{-1}. The *exo*-configuration is assigned to (**4**) on the basis of the similarity of the triplet signal of H-4 with that of the axial proton of (**5**) or (**6**). In contrast, the signal of the equatorial proton of (**6**) is a broad singlet. In the presence of 0·06 mol. equiv. of $SbCl_5$, 40% of the *cis*-tetraoxan (**6**) rearranges to the *trans*-isomer (**5**) during 30 min. When this reaction was performed using (**4**) under the same conditions, only the *trans*-isomer (**5**) was obtained in a yield of 89%, which suggests that (**4**) is not the precursor of (**6**).



(**7**) (**8**)

a; $R^1 = R^2 = Ph$
b; $R^1 = R^2 =$ n-pentyl
c; $R^1 = Ph$, $R^2 =$ n-pentyl

The formation of tetraoxans from ozonides seems to be quite general. The trioxalan (**7a**) gave the corresponding tetraoxan (**8a**) m.p. 201—202 °C (lit.[5] 202 °C) in 40% yield with $SbCl_5$ and in 41% yield with $ClSO_3H$.† (**7b**) gave (**8b**) in 35% yield with $SbCl_5$;† ^{1}H n.m.r., δ 5·68 (2H, t, *J* 4·5 Hz). Compound (**7c**) gave a mixture of the tetraoxans (**8a**) (4%), (**8b**) (13%), and (**8c**)† (27%); δ 6·02 (1H, t, *J* 4·8 Hz) and 6·68 (1H, s), with $SbCl_5$. In all these reactions the corresponding carbonyl compounds were isolated as by-products.

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