Synthesis of 1,2-Dioxacyclopentanes

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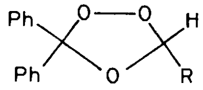
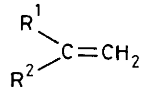
The reactions of a number of ozonides and olefins in the presence of boron trifluoride–diethyl ether gave the corresponding 1,2-dioxacyclopentanes in 21—77% yield.

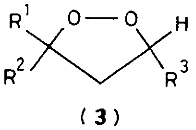
Of relevance to prostanoid endoperoxide, synthesis of 1,2-dioxacyclopentanes has attracted great attention.[1–6] While developing a general synthetic method for cyclic peroxides from ozonides,[7–9] we discovered that the reactions of the ozonides triphenylethylene ozonide (**1a**) or 1,1-diphenylhept-1-ene ozonide (**1b**) with the olefins 2-methylpent-1-ene (**2a**), methylenecyclohexane (**2b**), α-methylstyrene (**2c**), or 1,1-diphenylethylene (**2d**) in the presence of boron trifluoride–diethyl ether gave the corresponding 1,2-dioxacyclopentanes, as shown in Table 1. The following experimental procedure illustrates the method.



(**1**)
a; R = Ph
b; R = Pentyl



(**2**)
a; R^1 = Pr, R^2 = Me
b; R^1, R^2 = $-[CH_2]_5-$
c; R^1 = Ph, R^2 = Me
d; R^1 = R^2 = Ph



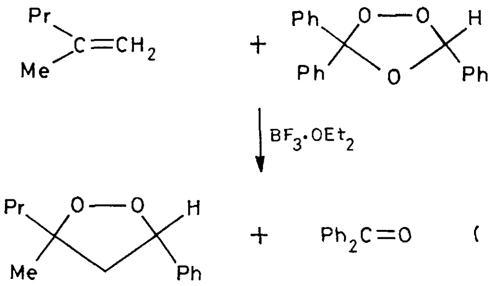
(**3**)
a; R^1 = Pr, R^2 = Me, R^3 = Ph
b; R^1, R^2 = $-[CH_2]_5-$, R^3 = Ph
c; R^1 = R^3 = Ph, R^2 = Me
d; R^1 = R^2 = R^3 = Ph
e; R^1, R^2 = $-[CH_2]_5-$, R^3 = Pentyl
f; R^1 = Ph, R^2 = Me, R^3 = Pentyl

To a solution of $BF_3 \cdot OEt_2$ (2 mmol) in dichloromethane (5 ml) was added a mixture of (**1a**) (2 mmol) and (**2a**) (2 mmol) in dichloromethane (10 ml) in one portion, and the mixture was stirred at 0 °C for 20 min. After conventional work-up the products were isolated by column chromatography on silica gel using benzene–light petroleum as eluant. The first

Table 1. Synthesis of 1,2-dioxacyclopentanes.[a]

Ozonide (**1**)	Olefin (**2**)	1,2-Dioxacyclopentane (**3**)[b] Yield/mol %
a	a	a[d] 34
a	b	b 21
a	c	c[d] 77
a	d	d[c] 32
b	b	e 21
b	c	f[d] 39

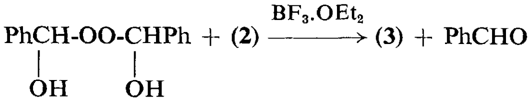
[a] All the products gave satisfactory spectral and elemental analysis data. [b] The products were obtained as liquids unless otherwise noted. [c] M.p. 63—65 °C (from methanol; lit.[4] 66 °C). [d] An equimolar mixture of *cis*-and *trans*-isomers.



(1)

fraction contained 3-methyl-3-propyl-5-phenyl-1,2-dioxacyclopentane (**3a**) (34% yield; an equimolar mixture of *cis*- and *trans*- isomers). From the second fraction benzophenone was obtained in a yield of 85% [equation (1)]. Elaborate column chromatography of (**3a**) on silica gel has enabled us to isolate both isomers in pure states. One isomer, eluted first, has the following characteristics; i.r. ν_{max} (neat) 1450, 1370, 750, and 690 cm^{-1}; ^{1}H n.m.r. ($CDCl_3$) δ 0.95 (3H, t, J 6.3 Hz), 1.39 (3H, s), 1.34—1.85 (4H, m), 2.30 (1H, 2 × d, J 12.0 and 7.8 Hz), 2.83 (1H, 2 × d, J 12.0 and 7.8 Hz), 5.22 (1H, t, J 7.8 Hz), and 7.20—7.68 (5H, m); *m/e* 206 (M^+). The physical properties of the second isomer are as follows; i.r. ν_{max} (neat) 1450, 1370, 750, and 690 cm^{-1}; ^{1}H n.m.r. ($CDCl_3$) δ 0.91 (3H, t, J 7.2 Hz), 1.35 (3H, s), 1.18—1.90 (4H, m), 2.36 (1H, 2 × d, J 12.0 and 7.8 Hz), 2.69 (1H, 2 × d, J 12.0 and 7.8 Hz), 5.26 (1H, t, J 7.8 Hz), and 7.14—7.74 (5H, m); *m/e* 206 (M^+).

Bis(α-hydroxybenzyl) peroxide (**4**) can also be used successfully in place of (**1a**); the reaction of (**4**) with (**2a**) or (**2c**) in the presence of $BF_3 \cdot OEt_2$ afforded (**3a**) (*cis*: *trans* = 1 : 1) and (**3c**) (*cis* : *trans* = 2 : 3)[4] in yields of 32 and 48%, respectively [equation (2)].



$$\underset{\substack{|\\ OH}}{PhCH}\text{-}OO\text{-}\underset{\substack{|\\ OH}}{CHPh} + (\mathbf{2}) \xrightarrow{BF_3.OEt_2} (\mathbf{3}) + PhCHO \qquad (2)$$

(**4**)

These results demonstrate that in the presence of an acid catalyst compounds (**1a**), (**1b**), or (**4**) act as the equivalent of the corresponding hypothetical carbonyl oxide (benzaldehyde or hexanal *O*-oxides) in an apparent [3 + 2] cycloaddition with olefins leading to dioxacyclopentanes.

Received, 31st December 1981; Com. 1493

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