Products and kinetics of the thermal decomposition of (L-(−)-menthyl)[2,2′-methylene-bis-(4-methyl-6-*tert*-butylphenyl)] phosphite ozonide

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Two conformers (chair, boat) of [L-(−)-menthyl)]-[2,2′-methylene-bis-(4-methyl-6-*tert*-butylphenyl)] phosphite ozonide have been obtained by the low temperature ozonization (−80 °C) of [L-(−)-menthyl)]-[2,2′-methylene-bis-(4-methyl-6-*tert*-butylphenyl)] phosphite. It was determined that decomposition of the ozonide is first order with the rate constant $\log k_0 = (10.92\pm1.10)-(14.02\pm1.25)/\theta$ ($\theta = 2.303RT$, kcal mol^{-1}), leading to [L-(−)-menthyl)]-[2,2′-methylene-bis-(4-methyl-6-*tert*-butylphenyl)] phosphate and oxygen (including singlet oxygen). Conformational transitions (chair—boat) for [L-(−)-menthyl)]-[2,2′-methylene-bis-(4-methyl-6-*tert*-butylphenyl)] phosphate have been registered by ^{31}P NMR spectroscopy.

Key words: phosphite ozonides; ^{31}P NMR spectra.

The interaction of ozone with phosphites at low temperatures (≤−80 °C) gives rise to phosphite ozonides.[1] Ozonides of triaryl phosphites are found to be much more stable than ozonides of trialkyl phosphites.[1,2] There is practically no information concerning ozonides of mixed alkyl-aryl phosphites, including those that are optically active.[3] At the same time, the study of such ozonides is very important, because optically active ozonides can be used as chiral oxidizing agents

Experimental

^{31}P NMR spectra were recorded with H_3PO_4 as the internal standard using a Bruker CXP spectrometer. Mass spectra were obtained using a MX-1320 mass spectrometer. Optical rotations were measured with a Perkin—Elmer 241 MC polarimeter using a cell (length: 1 dm) with temperature control.

L-(−)-Menthol. $[\alpha]_D^{22}$ −40° (CH_2Cl_2). The substance was isolated from menthol oil according to the procedure reported previously,[4] and distilled twice *in vacuo*. Dichloromethane was purified by passing it through a column of alumina, and was distilled and dried over 4 Å molecular sieves.

[L-(−)-Menthyl)]-[2,2′-methylene-bis-(4-methyl-6-*tert*-butylphenyl)] phosphite (1) was obtained from 2,2′-methylene-bis-(4-methyl-6-*tert*-butylphenyl)phosphorochloridite and L-(−)-menthol. A three-necked flask equipped with a mechanical stirrer, reflux condenser, and dropping funnel was charged with 2,2′-methylene-bis-(4-methyl-6-*tert*-butylphenyl)phosphorochloridite (10 g) in benzene (100 mL). The mixture was heated to 30—40 °C with stirring, then a mixture of L-(−)-menthol (3.86 g) and pyridine (1.95 g) in benzene (25 mL) was added dropwise for a period of 1h. Then the solution was heated to 80 °C and stirred for 5—6 h. The precipitated salt was filtered off, the solvent was distilled off at reduced pressure; and the reaction mass crystallized. The latter was precipitated from acetone to give compound **1** (7 g, yield 54 %), $[\alpha]_D^{22}$ −40° (CH_2Cl_2), m.p. 183 °C. ^{31}P NMR spectrum: +135 ppm (−80 °C), mass spectrum, *m/z*: 524 [M$^+$]. Found (%): C, 76.64; H, 9.41; O, 7.99; P, 5.96. $C_{33}H_{48}O_3P$. Calculated (%): C, 75.57; H, 9.35; O, 9.16; P, 5.92.

Ozonide of [L-(−)-menthyl)]-[2,2′-methylene-bis-(4-methyl-6-*tert*-butylphenyl)] phosphite (2). An ozone-oxygen mixture (2 % ozone) was bubbled for 4—10 min through a solution of **1** in CH_2Cl_2 at −80 °C in a termostatted reactor (10 mL capacity). The velocity of feed of the O_3—O_2-mixture was 40—100 mL min^{-1}; the volume of the sample being ozonized was 2—10 mL. The solutions obtained were thoroughly flushed and stored in the dark at the temperature of liquid nitrogen.

[L-(−)-menthyl)]-[2,2′-methylene-bis-(4-methyl-6-*tert*-butylphenyl)] phosphate (3). The solution of ozonide 2 was allowed to warm to ambient temperature, the solvent was distilled off, and the crude product was purified by HPLC to give compound **3**, m.p. 73 °C, $[a]_D^{22}$ −39° (CH_2Cl_2). Found (%): C, 72.08; H, 9.58; O, 12.98; P, 5.36. $C_{33}H_{48}O_4P$. Calculated (%): C, 73.33; H, 9.07; O, 11.85; P, 5.75.

The kinetics of the thermal decomposition of ozonide **2** was monitored by oxygen evolution. A glass thermostatted reactor (volume: 40 mL) equipped with an efficient mechanical stirrer was charged with CH_2Cl_2 (10 mL) saturated with oxygen. After the temperature reached the desired value, compound **2** (0.5—1 mmol) in CH_2Cl_2 (2 mL) was added and the volume of oxygen evolved was monitored. In addition the kinetics was monitored by chemiluminescence in the IR region

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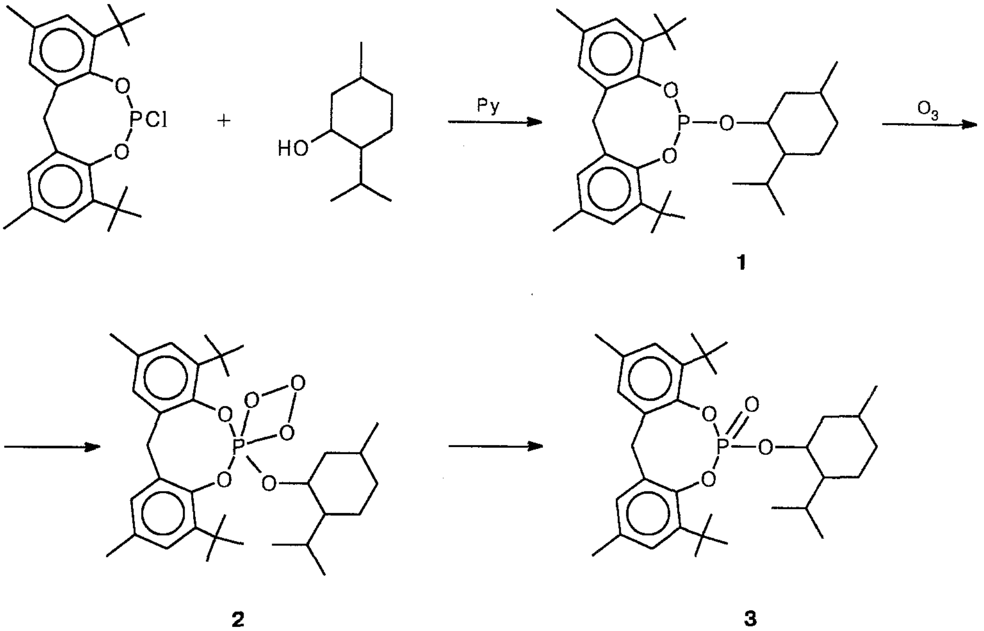
Scheme 1



using a procedure similar to one described earlier.[5] To do this, the reactor was charged with CH_2Cl_2 (10—20 mL), flushed with argon, the temperature was allowed to reach the desired value, and then ozonide **2** (0.5—1 mmol) in CH_2Cl_2 (2 mL) was added. An FEU-83 photomultiplier (registration region 1000—1300 cm^{-1} after correction for the IKS-7 filter) cooled to −60 °C was used as the light receiver.

Results and Discussion

The primary product of the reaction between **1** and ozone is the ozonide **2**, which is rather stable at temperatures $\leq$−80 °C. The typical ^{31}P NMR spectrum of the crude product of the ozonization of **1** comprises two groups of lines. The low field signals (−10 and −13 ppm) belong to compound **3**. These high field signals (−48, −59 and −63 ppm) are typical for ozonides (the chemical shifts of phosphite ozonides are in the region of −37÷122 ppm).[1,6] The signals at −59 and −63 ppm belong to the different conformations of the ozonide: chair (**2a**) or boat (**2b**). However, conformational transitions **2a** $\rightleftharpoons$ **2b** could not be observed because when the temperature was increased the ozonide rapidly decomposed (as will be shown below, conformational changes of this type can be easily detected for [L-(−)-menthyl)]-[2,2′-methylene-bis-(4-methyl-6-*tert*-butylphenyl)] phosphate, the product of the decomposition of **2**). The difference in the chemical shifts of **2a** and **2b** is 4 ppm; this value is close to that of the different phosphate conformers (3 ppm).

The resonance signal at −48 ppm is situated at much lower field than those of conformers **2a** and **2b**. Hence, this signal is not related to conformational changes in the ozonide molecule. It probably belongs to the dimeric ozonide **2c**, whose structure has been proposed.[7] A hypothesis concerning the formation of dimeric ozonides has been suggested earlier.[1,7,8] However, no experimental evidence was presented in the cited references. The ^{31}P NMR spectrum indicates that the concentration of the monomeric ozonide is much higher than that of the

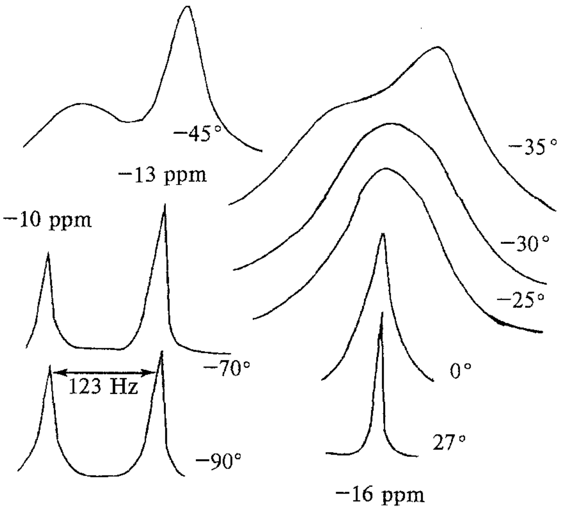
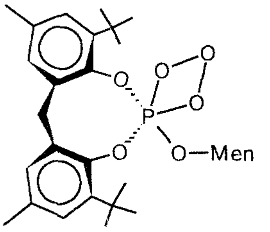
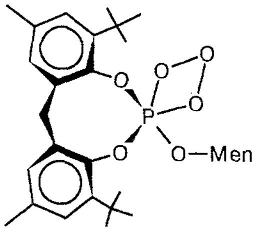


Fig. 1. ^{31}P NMR spectra of compound **3** in CH_2Cl_2 at various temperatures.

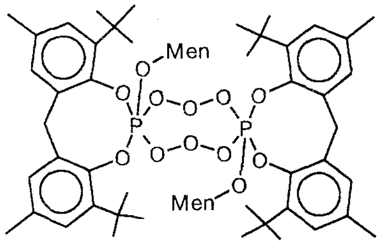
dimeric form. Thus, after ozonization of **1** (−80 °C, initial concentration of **1** — 0.2 mol L^{-1}) the ratio of the integral intensities of the signals of the dimeric and monomeric ozonides is 1:9.



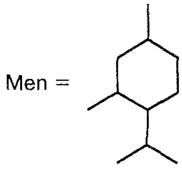
2a



2b



2c



Kinetics of the thermal decomposition of 2. According to the kinetic data, the overall decomposition of **2** in CH_2Cl_2 can be described by a first order law:

$$-d[\mathbf{2}]/dt = k_0[\mathbf{2}] ,$$

where k_0 is the first order rate constant.

From the dependence of k_0 on temperature:

T/°C	$k_0 \cdot 10^{-3}$/s^{-1}	T/°C	$k_0 \cdot 10^{-3}$/s^{-1}
−42	3.02	−16.5	92.10
−34	10.50	−12	127.00
−32	19.50	−4	290.00
−28	33.20		

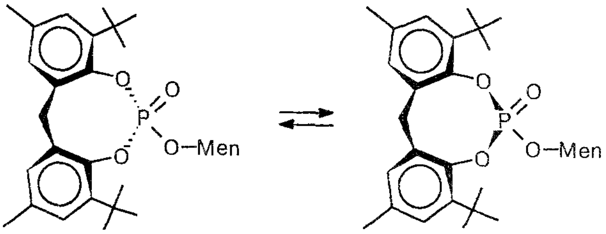
it was found that

$$\log k_0 = (10.92\pm1.10)-(14.02\pm1.25)/\theta \ s^{-1},$$

where $\theta = 2.303\ RT$ (kcal mol^{-1}).

Decomposition products. At the temperatures above −70 °C considerable decomposition of the ozonide 2 is observed. Oxygen evolution is evidence for this process. A typical acceptor of singlet oxygen ($^1O_2$), tetraphenylfuran (TPF), is rapidly oxidized in the presence of decomposing 2 (Δ[TPF]/Δ[2] = 0.6 mol mol^{-1}, where Δ[TPF] and Δ[2] are the amounts of the furan reacted and the ozonide decomposed, respectively). This indicates that $^1O_2$ is generated in the process of thermolysis of the ozonide. The intense chemilumenescence in the IR region (1000—1300 nm) detected during the decomposition of compound **2**, is additional evidence of $^1O_2$ formation (*cf.* Ref. 9).

Another product of the decomposition of ozonide **2** is [L-(−)-menthyl)]-[2,2′-methylene-bis-(4-methyl-6-*tert*-butylphenyl)] phosphate, which exhibits a signal in the ^{31}P NMR spectrum at −16 ppm. As the temperature decreases the line broadens reversibly and is subsequent split into two signals (the coalescence temperature is −30 °C, see Fig. 1). This spectral change seems to be related to a chair—boat type conformational transition.



The rate constant (k_0) and the energy barrier ($\Delta G^{\neq}$) for the observed process of structural change at the coalescence temperature are equal to $3 \cdot 10^2\ s^{-1}$ and 11 kcal mol^{-1}, respectively. These values were calculated according to a published procedure;[10] the value of $\delta\nu$ = 123 Hz (−90 °C) was used in the calculation).

It should be noted that such conformational transitions are not observed if the bulky menthyl group is replaced with a smaller phenyl group. ^{31}P NMR spectra (−80 °C, ppm): −62 (s) phenyl-[2,2′-methylene-bis-(4-methyl-6-*tert*-butylphenyl)] phosphite ozonide; −16 (s) phenyl-[2,2′-methylene-bis-(4-methyl-6-*tert*-butylphenyl)] phosphate.

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