CONCLUSIONS

Oxidation of 2,4-diaminoazobenzene and its 5-methyl- and 5-butoxyderivatives with oxygen in the system copper(I) chloride—pyridine gives, in addition to polymers, mixtures of the corresponding bis(2-phenyl-1,2,3-triazolo)[4,5a:4'5'h]phenazines and bis(2-phenyl-1,2,3-triazolo)[4,5c:4'5'g]-9,10-diazaphenanthrenes.

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ISOLATION AND INVESTIGATION OF THE THERMAL STABILITY OF THE OZONIDE OF [L(—)-MENTHYL][o-PHENYLENE] PHOSPHITE

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The low-temperature ($\sim$80°C) ozonization of esters of phosphorous acid leads to the ozonides of phosphites $(RO)_3P\cdot O_3$ [1]. These compounds are highly effective oxidants [1-4], and are sources of singlet oxygen [5]. There is no information in the literature concerning the isolation of ozonides from optically active phosphites. Moreover, the optically active ozonides may present interest as chiral oxidants.

The aim of the given work is to isolate the optically active ozonide of [L(−)-menthyl] [o-phenylene] phosphite and to study its thermal stability.

EXPERIMENTAL

The L(−)-menthol having the $[\alpha]_D^{22°}$ of −40.0° (CH_2Cl_2) was isolated from menthol oil according to the method of [6]; it was distilled twice *in vacuo*. The CH_2Cl_2 was purified by passage through a column with Al_2O_3, distilled, and dried over a molecular sieve of the 4 Å type.

[L(−)-Menthyl][o-phenylene] Phosphite (I). This was synthesized by the reaction of o-phenylenephosphino chloride with L(−)-menthol by the method analogous to the isolation of ethyl o-phenylene phosphite, having the bp 166-168°C (8 mm) using n-hexane [7] as the solvent [7]. The IR spectrum (ν, cm^{-1}) was as follows 840 (P—OC aryl), 1245 (P—OC aryl), 2880, 2935, and 2965 (C—H, CH_2, CH_3). The PMR spectrum ($CDCl_3$, δ, ppm, J, Hz) was as follows: 7.31 m (4H), 3.67 m (CH—O, J ≈ 10; 6.5; 4), 1.81-2.25 m ($C\underline{H}$—CH_3, CHO—$C\underline{H}$), 1.6 m (CHO—$C\underline{H}_2$, $C\underline{H}(CH_3)_2$), 0.9-1.27 m (CH_2, 4H), 0.7, 0.81, and 0.92 d (CH_3, 9H). The ^{13}C NMR spectrum ($CDCl_3$, δ, ppm) contains the signals of three methyl groups (15.56; 20.94; 21.98), three methylene groups of the cyclohexane ring (44.04; 33.90; 22.71), four methine carbon atoms of the isopropyl group (25.4) and the cyclohexane ring (31.60; 48.26, $J_{^{31}P}$ = 2.93 Hz; 76.89, $J_{^{31}P}$ ≈ 2 Hz), and the signal of double intensity for the four carbon atoms of the

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benzene ring (111.92; 122.36). The two carbon atoms of the benzene ring, which are connected to the P–O group, have the following chemical shifts and splitting constants of ^{31}P (ppm): 145.83 (J = 6.8 Hz) and 145.35 (J = 6.9 Hz). The signal with reference to H_3PO_4 is at 131 ppm. Found: C 65.76; H 8.13, O 15.54, and P 10.52%. Calculated: C 65.31, H 7.82, O 16.33, and P 10.54%.

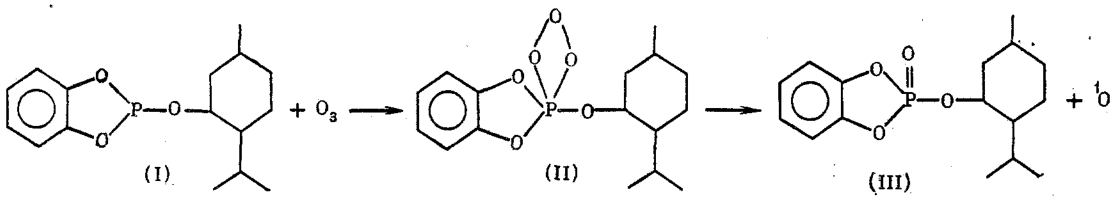
Ozonide of [L(−)-Menthyl][o-phenylene] Phosphite (II). An ozone–oxygen mixture (1.5% O_3) was passed through the solution of (I) in CH_2Cl_2 ($1\cdot10^{-2}$ M) at −80°C in a narrow (1 cm) thermostatted Pyrex reactor (10 ml capacity) for 4-10 min. The rate of inflow of the O_3–O_2 mixture was 30-40 ml/min; the volume of the sample being ozonized was 4 ml.

The angles of rotation of α-L(−)-menthol, [L(−)-menthyl][o-phenylene] phosphite, the ozonide of [L(−)-menthyl][o-phenylene] phosphite, and its decomposition products were determined on a Perkin–Elmer 141 polarimeter in a thermostatted cuvette of length 1 dm. For the measurement of α-(II), the cuvette was rapidly filled with its solution prior to thermostatting it at 0°C and recording the reading of the instrument. The procedure of filling the cuvette, the thermostatting, and the measurement took 5 min (it is shown below that the lifetime of (II) at 0°C comprises 40 min). The specific rotation $\alpha_D{}^t$ was calculated according to [8].

The kinetics of the thermal decomposition of (II) were investigated gasometrically and by the method of chemiluminescence (CL). For the registration of the CL, the solution of (II) (10^{-3} M) in CH_2Cl_2 was placed in a thermostatted reactor (0-30°C) of volume 50 ml in an atmosphere of Ar. The intensity of the CL was measured on apparatus analogous to [9]. The light detector utilized was FEU-83, which is sensitive in the IR region; the region of registration was 1000-1300 nm with the IKS-7 light filter. The IR spectra were recorded on the UR-20 spectrometer. The ^1H, ^{13}C, and ^{31}P NMR spectra were obtained on the Tesla BS-567A (100 MHz), Jeol FX-90a (22.5 MHz), and NMR SKhR Bruker instruments correspondingly.

DISCUSSION

When the ozone–oxygen mixture is passed, at −80°C, through the solution of (I) in CH_2Cl_2, the effective absorption of the O_3 occurs; the passage of ozone is only observed with the virtually complete conversion of the phosphite. The primary product of this reaction is the ozonide (II).



The identification of the ozonide and its decomposition product – the phosphate (III) – was carried out by the method of ^{31}P NMR according to the presence of signals with the chemical shift of −33.0 and +13.7 ppm correspondingly in the spectrum.

The specific rotation of the initial phosphite ($[\alpha]_D{}^0$) was −40.0°; the specific rotations of the obtained ozonide and its decomposition product were −40.0° and −34.5° respectively.

The heating of (II) from −80°C to ~+20°C leads to the intensive release of $^1O_2$. This is indicated by the intense chemiluminescence in the IR region at 1000-1300 nm, arising in the thermolysis of (II); it is well known [10] that $^1O_2$ has a characteristic emission spectrum with a maximum at 1270 nm. Another particular line of evidence for the formation of $^1O_2$ in the thermal decompostion of (II) is the quenching in the process of the luminescence by a typical acceptor of $^1O_2$ such as 2,3,4,5-tetraphenylfuran.

The ozonides of phosphites are unstable compounds [1] and, consequently, it is necessary to know their thermal stability for their successful application as oxidants. According to the data of the study of the kinetics of the thermolysis of (II) in CH_2Cl_2, the rate of its decomposition is described by the equation of first order

$$-d[(RO)_3P\cdot O_3]/dt = k_d[(RO)_3P\cdot O_3]$$

From the temperature dependence of the rate constant (k_d) of the decomposition of (II)

t, °C	0	5	10	20	28
$10^3 k_d$, sec^{-1}	0.4	1.7	1.0	2.7	6.7

it is found that

$$\log k_d = (7.96 \pm 2.63) - \frac{(14.03 \pm 3.43)}{\theta}, \text{ sec}^{-1}$$

where $\theta = 2.303 \cdot RT$, kcal/mole.

The comparison of the stability of the ozonide of [L(−)-menthyl][o-phenylene] phosphite and the ozonide of triphenyl phosphite [the utilization of $(C_6H_5O)_3P \cdot O_3$ as an oxidant is well known [1-4]] shows that (II) is significantly more stable. The lifetimes of (II) and $(C_6H_5O)_3P \cdot O_3$ comprise 42 and 2 min (0°C) correspondingly.

CONCLUSIONS

The optically active ozonide of [L(−)-menthyl][o-phenylene] phosphite was obtained; its thermal stability was studied.

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