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DECOMPOSITION OF TRICYCLOHEXYLIDENE PEROXIDE

E. K. Starostin, A. V. Aleksandrov,

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A. V. Ignatenko, and G. I. Nikitin

Cycloalkanes and lactones [2, 3] are formed in the thermal and photolytic decomposition of cyclic peroxides which are synthesized from cycloalkanones and H_2O_2 [1] Thus, the thermal decomposition of tricyclohexylidene peroxide (I) leads to cyclopentadecane (II) and the hexadecanolide (III) in amounts of 0.15 and 0.25 mole per mole of (I):



In the present work the thermolysis of (I) has been investigated with the aim of establishing the structure of the "dilactone" postulated in [4] and answering some questions related to the reaction mechanism. The composition and yield of the products obtained in the thermolysis of (I) in octanoic acid at 180°C are given in Table 1. These data show that the dilactone (IV) is formed together with the macrolactone (III) [(III) : (IV) \approx 4:1]



The structure of the preparatively isolated dilactone (IV) was confirmed by ¹H and ¹³C NMR and by IR and mass spectrometry. 1,10-Decanedicarboxylic acid is formed in the hydrolysis of (IV). However, the pres-

TABLE 1. Products of the Thermal Decomposition of Tricyclohexylidene Peroxide (I) in Octanoic Acid*

Products	Yield, moles/ mole peroxide	Products	Yield, moles/ mole peroxide
Cyclopentadecane	0,40	Cyclopentane	0,04
Hexadecanolide	0,12	Hexanoic acid	0,03
Dilactones (IV) and (V)	0,03	ε-Caprolactone	0,08
Cyclohexanone	0,19	CO ₂	1,60

*Oxygen and pentadecene were identified qualitatively.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 141-144, January, 1982. Original article submitted June 11, 1981.



Fig. 1. EPR spectrum of the radicals formed in the UV irradiation of tricyclohexylidene peroxide at -196° C.

ence of two signals in the ¹³C NMR spectrum in the region 64.4 and 64.1 ppm, which corresponds to the ¹³CH₂O groups, can indicate the presence of the isomeric dilactone (V). Based on the integral intensities, (IV): (V) \approx 8:1. Besides the macrocyclic compounds (II)-(V), cyclopentane, ε -caprolactone, hexanoic acid, and cyclo-hexanone were found in the decomposition products (see Table 1), and pentadecene and oxygen were identified qualitatively.

In order to clarify the mechanism of formation of the reaction products, EPR was applied to the photolytic decomposition of (I). However, the results obtained apply to a certain degree also to the thermal decomposition of this peroxide, since the identical products are obtained in the photolysis and thermolysis [5]. In the photolysis of frozen solutions of (I) in octanoic acid (-196°C) radicals of the type of RCH₂CH₂ appear, the spectrum of which (see Fig. 1) consists of six components with the mean hfs splitting between them $a_{\rm H} \approx 22$ Oe and a ratio of intensities 1: 3: 4: 4: 3: 1. The broadening of the components is probably due to the formation of radicals of the type RCH₂CH₂...CH₂CH₂R, located close to each other (~ 8-10 Å), leading to the appearance of spin-spin coupling. The broadening of the components also indicates the presence of biradicals $\dot{C}H_2(CH_2)_n\dot{C}H_2$ (n = 3 or 13), which are further converted to cyclopentane or cyclopentadecane

$$\dot{C}H_2(CH_2)_n\dot{C}H_2 \longrightarrow (CH_2)_{n+2}$$

 $n = 3. 43$

Besides this, the radical mechanism of the reaction is confirmed by data on the proton CIDNP of the compounds formed in the thermal decomposition of (I) in DMSO. The observed CIDNP effects are similar to the CIDNP effects of the decomposition products of dicyclohexylidene peroxide [6]. The multiplet polarization E/A in the region 4.8-5.6 ppm corresponds to the protons of the C = C end bond and belongs to pentadecene, a product of the disproportionation of the pentadecane biradical

$$\dot{C}H_2(CH_2)_{13}\dot{C}H_2 \rightarrow CH_2 = CH - (CH_2)_{12} - CH_3$$

Cyclopentadecane, which is a product of intracellular cyclization, is not polarized, since in the biradical $\Delta g \approx 0$, and the multiplet polarization does not appear since all protons are equivalent. CIDNP of the protons of the CH₂OC(O) group could have been expected in the mono- and the dilactone; however, it was not observed, as in the case of the diperoxide [6], apparently due to the short life of the corresponding biradicals.

Based on the data obtained, the mechanism of decomposition of tricyclohexylidene peroxide (I) can be presented in a general form. Most probably, the decomposition starts with the rupture of one of the O-O bonds and the rearrangement of the alkoxy radicals into biradicals (A); by recombination these are then converted to intermediate decane-1,10-dioylcyclohexylidene peroxide (VI)



The subsequent decomposition of the peroxide (VI) leads to the biradicals (B). By liberating three, two, or one molecule of CO_2 , these biradicals are then converted to cyclopentadecane, the monolactone (III), and the dilactone (IV), respectively. Fragment radicals which have escaped from the "cage" are converted to hexanoic acid, cyclopentane, cyclohexanone, or ε -caprolactone.

EXPERIMENTAL

The PMR spectra were obtained on a Tesla BS-467 spectrometer; the ¹³C NMR spectra, on a Bruker WP-60 instrument (with TMS as the internal standard). The EPR spectra were obtained on an ÉPR-2 spectrometer of the Institute of Chemical Physics, Academy of Sciences of the USSR; the IR spectra, on a UR-20 instrument; and the mass spectra, on an MKh-1303 spectrometer. GLC analyses were made with an LKhM-8MD chromatograph with a flame-ionization detector. The columns used were 1 m × 3 mm, packed with 15% SE-30 and 12% bis(2-cyanoethyl) ether on Chromosorb W (60-80 mesh). The substances were identified by means of reference samples; the yields were determined by the internal standard method. CO_2 was determined gravimetrically.

Tricyclohexylidene peroxide (I) was synthesized by the method given in [7], mp 91°C (from CH_3OH). PMR spectrum (CCl_4 , δ , ppm): 1.50 m (6H, CH_2), 1.70 m (4H, CH_2COO).

The thermal decomposition of the peroxide (I) was carried out in octanoic acid (0.25 mole/liter) in Ar at 180°. During the thermal decomposition the temperature rose to 200°. When the reaction was finished (after 3 h), the reaction mixture was cooled and the products were analyzed by GLC. The EPR spectra were obtained by irradiation of the frozen solutions of (I) in octanoic acid (-196°) with the filtered light from a DRSh-250 lamp (240 nm < λ < 400 nm) in the resonator of the spectrometer. Having switched off the light source, the changes in the EPR spectra were recorded due to the increase in sample temperature. CIDNP was observed in the decomposition of (I) in octanoic acid were neutralized with Na₂CO₃, extracted with ether, dried with MgSO₄, and distilled. Cyclopentadecane, bp 120-130° (10 mm). PMR spectra (CCl₄, δ , ppm): 126 s (CH₂). Pentadecene was isolated together with pentadecane. PMR spectra (CCl₄, δ , ppm): 126 s (CH₂), 4.9 m (CH₂ = CH). Hexadecanolide, bp 81-82° (0.4 mm). PMR spectrum (CCl₄, δ , ppm): 1.30 br. s (26H, CH₂), 2.25 t (2H, CH₂COO, J = 6 Hz), 4.07 t (2H, OCH₂, J = 5.2 Hz). IR spectrum (ν , cm⁻¹): 1740 (C = O). Mass spectrum: M⁺ 254.

The dilactones (V) and (VI) were isolated from the reaction mixture by chromatography on silica gel. (Silica gel L-40/100), eluent CCl₄-ether (20:1). Mass spectrum: M^+ 298. PMR spectrum (CCl₄, δ , ppm): 1.30 br. s (14H, CH₂), 1.55 br. s (8H, OCH₂<u>CH₂</u> and OOCCH₂<u>CH₂</u>), 2.23 t (4H, CH₂C = O, J=6Hz), 4.05 t (4H, OCH₂, J = 5.2 Hz). ¹³C NMR spectrum (CDCl₃, δ , ppm): 174.1 (C = O), 64.4 (OCH₂), 64.1 (OCH₂), 34.6 (CH₂COO), 28.7 (CH₂CH₂CO), 27.9 (CH₂). IR spectrum (ν , cm⁻¹): 1740 (C = O), 2940, 2860, 1465 (CH₂), 1175, 1250 (C - O). The ratio of the integral intensities of the IR bands at 1740 cm^{-1} was (IV) : (III) = 2; this indicated the presence of two ester groups in the molecule of (IV).

CONCLUSIONS

In the thermolysis of tricyclohexylidene peroxide in the liquid phase a "dilactone" is formed, besides the earlier identified macrocyclic compounds (cyclopentadecane and hexadecanolide), which is the cyclic ester of 1,10-decanedicarboxylic acid and 1,5-pentanediol.

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ASYMMETRICAL NON-BRIDGED NITROGEN

27.* NEW, OPTICALLY ACTIVE 1-ALKOXY-2,2-BIS(TRIFLUOROMETHYL)AZIRIDINES

R. G. Kostyanovskii, G. K. Kadorkina, G. V. Shustov, I. I. Chervin,

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Sh. S. Nasibov, and S. V. Varlamov

In aziridines of the type $(CF_3)_2CCH_2NOR$, the chiral nitrogen pyramid has high configurational stability

[2]. Hence for $R = CMe(CO_2Me)_2$, there is a difference in the reactivities of the diastereotopic ether groups and, as a result, the monosubstitution products upon alkaline hydrolysis and ammonolysis are obtained in unequal amounts [3]. In the case of $R = CMe_2CO_2Me$ and CMe_2CO_2H , the aziridines could be resolved into antipodes according to a previously described method [1]. A study of the racemization of these compounds and the epimerization of analogs with $R = CMe(CO_2Me)CONH_2$ and $CMe(CO_2Me)CO_2Et$ showed a higher nitrogen inversion barrier [3] than for derivatives with less bulky substituents R = CHMeCOX, X = MeO and NH_2 [4]. This unexpected finding is not in accord with the concept of a lowered nitrogen inversion barrier with increasing substituent bulk [5]. In the present work, this anomaly, which was discovered in our laboratory, was confirmed for further examples.

The starting aziridine was synthesized by the scheme



We should note that prolonged maintenance, as indicated in our previous work [4], is not required for the addition of CH_2N_2 to (I). For example, only traces of (I) (as seen using thin-layer chromatography) remain after treatment of (I) with a twofold excess of CH_2N_2 in ether after only 1 h.

* For Communcation 26, see [1].

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