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THE THERMAL REARRANGEMENT OF BIS-(1-PHENYL-3,5-DI-TERT-BUTYL-2, 5-CYCLOHEXADIEN-4-ONE) PEROXIDE

EVIDENCE FOR HOMOLYTIC CARBON-OXYGEN FISSION IN A SYMMETRICAL PEROXIDE

Elmar R.Altwicker, Clinton D.Cook, Niles D.
Gilmour, Bruce E.Norcross and Daniel Simpson
Department of Chemistry, University of Vermont
Burlington, Vermont

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It has been shown[1] that bis-(1-tert-alkyl-3,5-di-tert-butyl-2, 5-cyclohexadien-4-one) peroxides decompose thermally by oxygen-oxygen fission. We wish to present first evidence for homolytic carbon-oxygen cleavage in the symmetrical peroxide, bis-(1-phenyl-3,5-di-tert-butyl-2,5-cyclohexadien-4-one) peroxide[2], (**1**). When **1** was decomposed neat at 150-160° or in solvents such as benzene or bromobenzene a red-purple color reminiscient of 2,6-di-tert-butyl-4-phenyl phenoxy[2] (**2**) was produced transiently. These colored solutions showed visible absorption at 488 $m\mu$ identical to that of **2**, prepared by oxidation of 2,6-di-tert-

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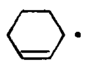
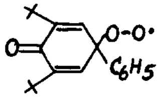
[1] C. D. Cook, R. C. Woodworth and P. Fianu, J. Am. Chem. Soc. 78, 4159 (1956)

[2] E. Müller, A. Schick and K. Scheffler, Chem. Ber. 92, 474 (1959)

butyl-4-phenyl phenol (3); 3 was isolated from these reactions. Qualitative tests with acrylonitrile indicated that 1 and/or its decomposition products did not initiate the polymerization of acrylonitrile at 70±3°, but did in fact inhibit the facile initiation of polymerization observed with bis-(1,3,5-tri-tert-butyl-2,5-cyclohexadien-4-one) peroxide. When 1 was decomposed *in vacuo* just below its melting point, 2 distilled (red-purple color of distillate, λmax 488 mμ, subsequent isolation of 3). A white crystalline solid (5) was isolated in variable yield from the vacuum as well as the solvent decomposition reactions. Preliminary kinetic data were obtained from a study of the decomposition of 1 in bromobenzene at 70°, 80°, and 90° by following the change in intensity of the 488 mμ absorption. From these data the activation energy for the cleavage of one carbon -oxygen bond has been estimated as 30 Kcal/mole.

From the reaction of 1 in refluxing cyclohexene a white crystalline solid (4), m. 164.0-5.2° (dec.) was isolated in 40% yield and 3 in 60% yield (these are minimum yields, based on the assumption that 1 mole 1 gives 1 mole 3; infrared data on the crude reaction mixture suggested that these yields may be 80-90%), after discharge of the red-purple color. The analytical and spectral data indicated that 4 resulted from the combination of a cyclohexenyl radical,  , with the peroxy radical  (this is not to be interpreted as a mechanism for the formation of **4**),(Calcd. for $C_{26}H_{34}O_3$: C 79.14, H 8.68, O 12.18; found C 79.03, H 8.48, O 12.17); λ max 231 mμ (ε 7.5 x 10^3), 358 mμ(ε 52); infrared bands at 3000, 2920, 1689, 1670, 1648, 1487, 1450, 1390, 1365, 1333; a series of sharp medium bands in the 1300-800 region; and strong bands at 762, 736, and 694cm.$^{-1}$.These data do not permit the assignment of an unambiguous structure to **4**. Compound **5** was not produced in this reaction, strongly suggesting that **5** (see below) is formed by a reaction path involving carbon-oxygen cleavage of **1**, and that cyclohexene is functioning as a peroxyradical trap.[3]

The neat decomposition of **1** at 150-160° for 3-5 min. proceeded with evolution of isobutylene and oxygen (identified by masspectroscopic analysis) and discharge of the red-purple color to give a yellow-orange glassy solid. Treatment with methanol or petroleum ether gave a small amount of **3** and **5**, m. 187.3-8.8°, in 70% yield; its elemental analysis and molecular weight agreed with **1** (calcd. for $C_{40}H_{50}O_4$: C 80.75, H 8.49, O 10.76, M.W. 594.4; found C 80.66, H 8.62, O 10.91 M.W. 593.8); λmax 236 mμ (ε 2.1 x 10^4), 276-8 mμ (ε 6.8 x 10^3)

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[3] M. S. Kharasch and A. Fono, J. Org. Chem. **24**, 72 (1959).

(plateau), 341m (ε 219). The infrared spectrum showed absence of OH and sharp strong bands at 3000, 2925, 1730, 1668, 1650, 1500, 1478, 1395, 1367, 1336; a series of sharp medium bands in the 1300-800 region, and strong bands at 760, 740, and 692cm^{-1}. The NMR-Spectrum showed single peaks at 9.04, 8.93 and 8.83 τ (tert-butyl groups), a doublet (J = 2 cps) at 6.29 τ (-O-$\overset{|}{\underset{|}{C}}$-H)[4], two unsymmetrical doublets (J = 2.5 cps) at 3.74 and 3.52 τ (vinyl-H)[4], and a single peak (with minor splittings) at 2.71 τ (aromatic H). Peak areas were in the ratios of 9:9:18:1:2:1:10. No exchange took place with D_2O. Based on these data and the degradation studies discussed below we propose for **5** the structure shown

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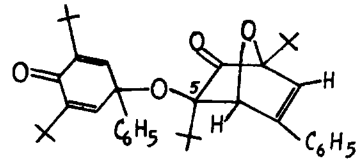

Above its melting point **5** decomposed slowly with gas evolution to give 76% **3** (assuming 1 mole **5** to give 1 mole **3**) and a complex mixture of products. Reduction with excess KI/ acetic acid at reflux gave 95% **3** and 67% 3-tert-butyl-5-phenyl catechol, m. 98.2-9.2°, (identified by elemental analysis, infrared, ultraviolet, and oxidation with PbO_2 to 3-tert-

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[4] These peaks are in the region reported by D. S. Tarbell et.al., J. Am. Chem. Soc. 84, 4115 (1962) for the 7-oxa-bicyclo-[2.2.1] heptene system.

butyl-5-phenyl-o-benzoquinone). Reduction with $LiAlH_4$ in refluxing tetrahydrofuran yielded better than 80% **3** and a mixture of isomers in 90% yield. Infrared[5] and ultraviolet[6] data suggested that this mixture consisted of 1,5-di-tert-butyl-5,6-dihydroxy-3-phenyl-7-oxabicyclo-[2.2.1] hept-2-enes.

The stereochemistry on carbon 5 in **5** has not been established. However, on the basis of a possible pathway[7] for the formation of **5** we favor the arrangement shown.

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[5] Reference 4 and private communication from Professor Tarbell.

[6] This isomeric mixture showed ultraviolet absorption at 257 mμ (log ε 2.7) in agreement with that reported by H. Wynberg, J.Am. Chem. Soc. 80, 364 (1958), for 3-phenyl-2,5-dihydrofuran, and at 252 mμ.

[7] Details on this as well as a detailed discussion of the structure of **5** will be published.