Vapor-Phase Thermolysis of Cyclic Malonyl Peroxides

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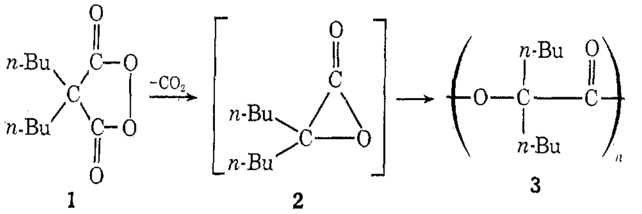
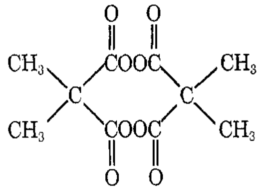
Recently Adam[1] has described an extensive study of the reactions of various peroxidic heterocycles, including cyclic malonyl peroxides. The major product of thermolysis or photolysis[2] of di(n-butyl)malonyl peroxide (**1**) in inert solvents is the polyester **3**. To



1 **2** **3**

account for this product the authors postulated the formation of the intermediate α-lactone **2**. Subsequently, α-lactonic intermediates were detected directly by photolysis of neat malonyl peroxide matrices at 77°K.[3]

In this note we wish to report tbe products of vapor-phase thermolysis of the dimeric dimethylmalonyl peroxide (**4**) and monomeric trimethylenemalonyl peroxide (**5**). The major products from both **4** and **5** are



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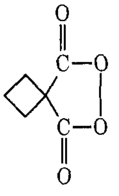
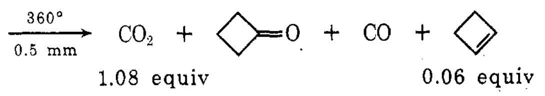


5

carbon dioxide and a ketone, acetone from **4** and cyclobutanone from **5**. Carbon monoxide was detected qualitatively. These three products are readily accounted for by the formation and subsequent decar-

$$\mathbf{4}\ \xrightarrow[0.5\ \text{mm}]{310°}\ \underset{2.2\ \text{equiv}}{CO_2} + \underset{1.8\ \text{equiv}}{(CH_3)_2CO} + CO + \underset{\text{presumed}}{CH_3CH{=}CH_2}$$

5



bonylation of an α-lactonic intermediate. Decarbonylation has previously been reported to be a primary photochemical reaction of α-lactones.[3]

The small amount of cyclobutene produced from **5** probably arises from a carbene intermediate derived from the decarboxylation of the α-lactone or from some intermediate leading to it. Adam and Rucktäschel also observed low yields of olefins from the liquid-phase photochemical decomposition of **1**.[2] Although propene, the olefin anticipated from **4**, was not actually detected, the yields of carbon dioxide and acetone suggest that approximately 10% of the α-lactone decomposed by loss of another unit of carbon dioxide. This process would generate dimethylcarbene, which would be expected to rearrange to propene.

Mass spectra suggest that the radical ions produced by electron-impact ionization of **4** and **5** may follow fragmentation sequences rather similar to the vapor-phase thermolysis. There are prominent signals at m/e values appropriate for species isomeric with the α-lactone (loss of CO_2), the ketone (loss of CO_2 and CO), and the alkene (loss of $2CO_2$), in addition to peaks due to CO_2 and CO. There is also a prominent signal corresponding to a species formed by loss of CO_2 plus O from the monomeric molecular ion, for which no analogous thermolysis product (a ketene) was detected. Finally, it is interesting to note that no molecular ion was detectable in the mass spectrum of **4**. The highest signal appears at m/e 130, the molecular weight of the monomeric cyclic peroxide. This suggests that the molecular ion of **4** is unstable and rapidly fragments by the process shown below. It is also possible that some of the signals observed in the mass spectra are due to ions formed from molecular species generated in thermal processes occurring in the inlet, although significant thermal decomposition seems rather unlikely considering the low inlet temperature (50–60°).

$$\underset{m/e\ 260}{[C_{10}H_{12}O_8]\cdot^+} \longrightarrow \underset{m/e\ 130}{[C_5H_6O_4]\cdot^+} + C_5H_6O_4$$

Experimental Section

Caution.—Although we experienced no problems in handling any of the materials described in this note, we urge that all of these peroxidic compounds, the 90% hydrogen peroxide in particular, be treated as potentially hazardous substances.

Dimethylmalonyl Peroxide (4).—To a chilled solution of 2.14 g (0.0165 mol) of dimethylmalonic acid in 10 g of sulfuric acid was added 2.2 ml of 90% hydrogen peroxide over 50–60 min. After 2 ml of cold saturated ammonium sulfate solution was added, the mixture was filtered and the solid was washed twice with 5-ml portions of cold saturated ammonium sulfate solution, dissolved in ether, and dried with magnesium sulfate. Removal of the ether and sublimation (0.1 mm, room temperature) gave 1.4 g (64%) of product: mp 48–49°; nmr ($CDCl_3$) τ 8.4 (sharp singlet); mass spectrum (25 eV, inlet temperature 60°) m/e (rel intensity) 130 (43), 86 (24), 70 (base peak), 58 (12), 44 (36), 42 (92), 28 (10); ir ($CHCl_3$) $\nu_{C=O}$ 1820 and 1804 cm^{-1} (shoulder). The ratio of intensities of the absorptions of 1820 and 1804 cm^{-1} was variable. Whether this was a consequence of some conformational equilibrium involving the peroxide, or was merely an artifact due to some minor impurity, was not established.

Anal. Calcd for $C_{10}H_{12}O_8$: C, 46.15; H, 4.61; active O, 12.31; mol wt, 260. Found: C, 46.28; H, 4.68; active O (titrimetric), 12.05; mol wt, 259 (ebullioscopic, methanol), 263 (Rast, camphene).

Trimethylenemalonyl Peroxide (5).[3]—This peroxide was synthesized in 56% yield by the same procedure described above: mp 63–64°; nmr ($CDCl_3$) τ 7.38 (broad, complex multiplet); mass spectrum (25 eV, inlet temperature 50°) m/e (rel intensity) 142 (50), 98 (20), 82 (64), 70 (29), 54 (73), 44 (base peak), 28 (64); ir ($CHCl_3$) $\nu_{C=O}$ 1803 cm^{-1}.

Anal. Calcd for $C_6H_6O_4$: C, 50.70; H, 4.23; active O, 11.26; mol wt, 142. Found: C, 50.81; H, 4.17; active O (titrimetric), 11.12; mol wt, 143 (ebullioscopic, $CHCl_3$).

Vapor-Phase Thermolysis.—A sample of the peroxide was sublimed through a 10 in. tube maintained at 310° for **4** and 360° for **5**, while a pressure in the apparatus of 0.4–0.5 mm was maintained. The flask from which the peroxide was sublimed

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[1] W. Adam, presented at the symposium on the Chemistry of Heterocyclic Compounds, Gordon Research Conference, New Hampton, N. H., June 30, 1972.

[2] W. Ad m and R. Rucktäschel, *J. Amer. Chem. Soc.*, **93**, 557 (1971).

[3] O. L. Chapman, P. W. Wojtkowski, W. Adam, O. Rodriquez, and R. Rucktäschel, *J. Amer. Chem. Soc.*, **94**, 1365 (1972).

was held at a temperature no higher than 26°. The effluent from the tube was passed through two traps, the first cooled in a Dry Ice–acetone bath, the second in liquid nitrogen. At the end of a pyrolytic run there was no residue in the flask from which the peroxide was sublimed, in the pyrolysis tube, or in areas of the apparatus which would experience intermediate temperatures, such as immediately preceding or following the pyrolysis tube. Thus there is no indication of the formation of any polyester analogous to **3** during vapor-phase pyrolysis.

Ketonic products were condensed in the Dry Ice–acetone bath. Acetone was identified by its retention time on glc, by coinjection with authentic acetone, and by conversion to its DNP derivative, mp 125–127° (lit.[4] mp 126°). The yield of acetone produced in the thermolysis was determined from the weight of DNP isolated. Cyclobutanone was identified by its retention time on glc, by coinjection with authentic cyclobutanone, and by conversion to its DNP derivative, mp 144–146° (lit.[4] mp 146°). Material collected in the Dry Ice–acetone trap exhibited no infrared absorption indicative of the presence of polyester analogous to **3**.

The yield of carbon dioxide was determined by venting the contents of the liquid nitrogen trap through a tube packed with Ascarite, and measuring the increase in weight.

Carbon monoxide was detected qualitatively be venting the contents of the liquid nitrogen trap through a solution of cuprous sulfate. An increase in weight signified the absorption of carbon monoxide.[5]

Cyclobutene was identified as a component of the contents of the liquid nitrogen trap by its retention time on glc, by coinjection with authentic cyclobutene, and by conversion to its Diels–Alder adduct with 1,3-diphenylisobenzofuran, mp 119–121°, identical with that of an authentic sample. The yield of cyclobutene was determined from the weight of the Diels–Alder adduct isolated.

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Registry No.—**4**, 40982-37-4; **5**, 34867-87-3; dimethylmalonic acid, 595-46-0; trimethylenemalonic acid, 5445-51-2; hydrogen peroxide, 7722-84-1.

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[4] Z. Rapporport, "Handbook of Tables for Organic Compound Identification," 3rd ed, Chemical Rubber Co., Cleveland, Ohio, 1967, p 161.

[5] A. E. Heron and H. N. Wilson in "Comprehensive Analytical Chemistry," Vol. 1A, C. L. Wilson and O. W. Wilson, Ed., Elsevier, New York, N. Y., 1959, p 243.

Kinetics of the One-Electron Transfer Reaction of Trimethyl Phosphite with Quinones[1]

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The reaction of trialkyl phosphite with quinones is well known.[3] For example, the reaction of *o*-quinones such as phenanthrenequinone and *o*-benzoquinone gives 1:1 adducts at room temperature,[4] while acenaphthenequinone gives a 2:1 adduct, which was produced by a rapid reaction of the 1:1 adduct with the second quinone molecule.[5,6] The reaction of *p*-quinones with trivalent phosphorus compounds yields reduction products of quinones, *e.g.*, *p*-alkoxyphenols *via* quinone-donor adducts.[7,8] The electron paramagnetic resonance spectrum was observed during the reaction of triethyl phosphite with chloranil,[9] but little is known about the detail of this phenomenon.

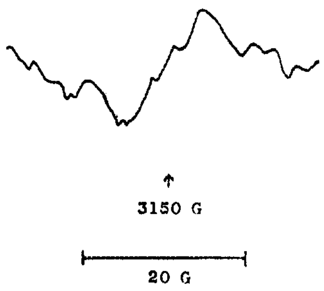


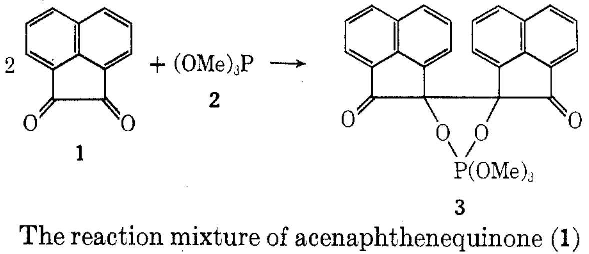
Figure 1.—Esr spectra obtained in the reaction of acenaphthenequinone with trimethyl phosphite in dioxane.

We have reported that the reaction of acenaphthenequinone with trimethyl phosphite caused the color change, the initiation of autoxidation of trimethyl phosphite, and polymerization of styrene,[10] which suggest the occurrence of radicals in the reaction. However, nothing is known on the mechanism of this radical formation and the relative amount of the radical formation and the relative amount of the radical product to the ionic product (a 2:1 adduct).

The present paper will describe further evidence and kinetics of the radical formation *via* one-electron transfer from phosphite to quinones to clarify its mechanism and the ratio of the radical to ionic paths. The paper will also describe the relation between the rate and the reduction potentials of some quinones.

Results and Discussion

As reported previously, the reaction of acenaphthenequinone (**1**) with excess trimethyl phosphite (**2**) at 25° under N_2 gave a 2:1 adduct of **1** and **2** [2,2,2-trimethoxy-4,5-biacenedionoxy-1,3,2-dioxaphospholane (**3**)] on the basis of its nmr and ir spectra.



(1)

The reaction mixture of acenaphthenequinone (**1**) and trimethyl phosphite (**2**) showed a red color shift. The color of DPPH vanished on addition of the reaction mixture, and the red color of the complex also disappeared. These observation suggest the presence of radicals.[10] On mixing **1** and **2** in dioxane, an esr signal was observed as shown in Figure 1. The rapid mea-

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[1] Contribution No. 194.

[2] To whom correspondence should be addressed.

[3] (a) R. F. Hudson, "Structure and Mechanism in Organo-Phosphorus Chemistry," Academic Press, London, 1965, p 187; (b) F. Ramirez, *Accounts Chem. Res.*, **1**, 168 (1968).

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[8] F. Ramirez and S. Dershowitz, *J. Amer. Chem. Soc.*, **78**, 5614 (1956).

[9] F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 856 (1957).

[10] Y. Ogata and M. Yamashita, *Bull. Chem. Soc. Jap.*, **46**, 2208 (1973).