

and evaporated in vacuo to give **36**⁴⁰ (2.67 g, 46%): bp 86–88 °C (0.3 mm); ν_{\max} 2930, 2850, 1695, 1645, 1430, 1390, and 1270 cm^{-1} ; NMR δ 2.65–1.85 (8 H, m) and 1.85–1.44 (4 H, m); M^+ m/e calcd for $\text{C}_9\text{H}_{12}\text{O}$ 136.089, found 136.089, in agreement with literature values.

Bicyclo[5.3.0]-9-decen-1-one (37). Cycloheptene-1-carboxyl chloride (4.80 g, 30 mmol) and vinyltrimethylsilane (3.34 g, 34 mmol) were treated with stannic tetrachloride (8.43 g, 34 mmol) under the same conditions as above to give, after workup, **37**⁴¹ (1.43 g, 32%): bp 91–94 °C (0.3 mm); ν_{\max} 2900, 2840, 1685, 1635, 1438, 1190, and 1055 cm^{-1} ; NMR δ 2.67–2.05 (8 H, m) and 2.05–1.15 (6 H, m); M^+ m/e calcd for $\text{C}_{10}\text{H}_{14}\text{O}$ 150.105, found 150.105, in agreement with literature values.

5-Isopropylbicyclo[4.3.0]-8-nonen-1-one (38). 4-Isopropylcyclohexene-1-carboxyl chloride (4.00 g, 22 mmol) and vinyltrimethylsilane (2.51 g, 25 mmol) in dry dichloromethane (50 mL) at –30 °C were treated with stannic tetrachloride (6.50 g, 25 mL) under the same conditions as above to give, after workup, **38** (2.20 g, 56%): bp 110–112 °C (0.5 mm); ν_{\max} 2960, 2920, 2870, 1700, 1650, 1395, and 1265 cm^{-1} ; NMR δ 2.66–1.85 (8 H, m), 1.85–1.20 (4 H, m) and 0.90 (6 H, d, $J = 7$ Hz); M^+ m/e calcd for $\text{C}_{12}\text{H}_{18}\text{O}$ 178.136, found 178.136.

7-Methylbicyclo[4.3.0]-8-nonen-1-one (39). 6-Methylcyclohexene-1-carboxyl chloride (5.70 g, 36 mmol) and vinyltri-

methylsilane (4.10 g, 40 mmol) in dry dichloromethane (40 mL) at –30 °C were treated with stannic tetrachloride (10.68 g, 40 mmol) under the same conditions as above to give, after workup, **39** (3.43 g, 63.5%): bp 100–102 °C (0.5 mm); ν_{\max} 2920, 2680, 1690, 1640, and 1390 cm^{-1} ; NMR δ 2.70–2.00 (7 H, m), 2.00–1.30 (4 H, m) and 1.12 (3 H, d, $J = 4.5$ Hz); M^+ m/e calcd for $\text{C}_{10}\text{H}_{14}\text{O}$ 150.105, found 150.105. The above fused cyclopentenones were $\geq 95\%$ pure (GLC).

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Registry No. 9, 72610-19-6; 10, 72610-20-9; 11, 72610-21-0; 12, 72610-22-1; 13, 72610-23-2; 14, 57682-85-6; 15, 54848-82-7; 16, 1822-73-7; 17, 16411-16-8; 18, 16336-54-2; 20, 72622-64-1; 21, 72622-65-2; 22, 72622-66-3; 23, 20451-53-0; 24, 62762-20-3; 25, 72622-67-4; 35, 10515-92-1; 36, 22118-00-9; 37, 769-32-4; 38, 72622-68-5; 39, 67220-96-6; (2,4-dinitrophenyl)sulfonyl chloride, 528-76-7; trimethylvinylsilane, 754-05-2; (2-nitrophenyl)sulfonyl chloride, 7669-54-7; phenylsulfonyl chloride, 931-59-9; *p*-(chlorothio)phenol, 72622-69-6; *p*-tolylsulfonyl chloride, 933-00-6; cyclopentene-1-carboxyl chloride, 59253-90-6; cyclohexene-1-carboxyl chloride, 36278-22-5; cycloheptene-1-carboxyl chloride, 72233-47-7; 4-isopropylcyclohexene-1-carboxyl chloride, 72622-70-9; 6-methylcyclohexene-1-carboxyl chloride, 72622-71-0; (4-chlorophenyl)sulfonyl chloride, 933-01-7.

Ozonolysis of Diphenylvinylene Carbonate. Synthesis and Thermolysis of Dibenzoyl Monoperoxycarbonate

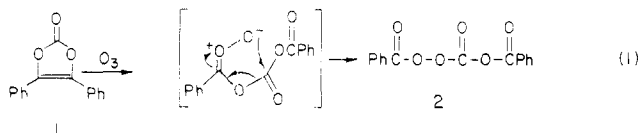
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Dibenzoyl monoperoxycarbonate (**2**) was prepared by the reaction of diphenylvinylene carbonate (**1**) with ozone. The thermolysis of **2** in benzene gives products typical of the formation of benzyloxy radicals. The reaction rate was investigated at different temperatures, and the activation parameters were determined ($\Delta H^\ddagger = 27.8 \pm 1.2$ kcal/mol, $\Delta S^\ddagger = 6.1 \pm 3.5$ eu). The thermolysis of **2** in the presence of the stable free radical galvinoxyl was investigated also. These experiments revealed that the fraction of radical escape from the solvent cage is $60 \pm 5\%$.

Ozonolysis of sterically hindered olefins in some instances gives epoxides as well as ozonides and their derived products.² In contrast, our attempt to epoxidize the hindered olefin diphenylvinylene carbonate (**1**) with ozone gave the unusual rearranged peroxide dibenzoyl monoperoxycarbonate (**2**). Peroxycarbonate **2**, to the best of



our knowledge, is the first reported example of a diacyl monoperoxycarbonate. Its formation is simply understood in terms of intramolecular trapping of the intermediate carbonyl oxide proposed by Criegee to be formed in the normal ozonation of olefins.³

Peroxide **2** is related to benzoyl peroxide in that it can be prepared conceptually by inserting CO_2 between the carbonyl and phenyl groups of that well-known peroxide.⁴ The products of the thermolysis of **2** in benzene are, in fact,

similar to those obtained from the thermolysis of benzoyl peroxide.⁵⁻⁷ However, the rate of reaction of **2** is significantly greater than that of benzoyl peroxide. The enthalpy and entropy of activation for the unimolecular decomposition of **2** suggest, moreover, that initial simultaneous two-bond cleavage occurs in this system.

Kiefer and Traylor⁸ have concluded that formation of small molecules between the *tert*-butoxy radicals that result from the thermolysis of di-*tert*-butyl peroxide, di-*tert*-butyl hyponitrite, or di-*tert*-butyl peroxyoxalate decreases the ratio of in-cage to cage-escaped products. Comparison of benzoyl peroxide and **2** expands this study since a molecule of CO_2 is formed between the benzyloxy radicals from **2**.

Results and Discussion

Synthesis. The addition of excess ozone to a solution of diphenylvinylene carbonate in CH_2Cl_2 gives, upon evaporation of the solvent, a peroxidic, colorless solid. In CCl_4 solution this product exhibits strong IR absorptions at 1853 and 1787 cm^{-1} . Since no other diacyl monoperoxycarbonates have been reported, it is not possible to

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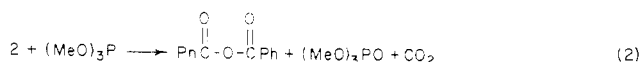
Table I. Products of Thermolysis of 2 in Benzene at 81.1 °C

product	yield ^a	CO ₂ balance ^b	radical balance ^c
CO ₂	2.0	2.0	
biphenyl	0.64		1.28
phenyl benzoate	0.05	0.05	0.10
benzoic acid	0.69	0.69	
residue ^d	0.54		1.08
		2.74 ^e	2.46 ^e

^a In moles of product/mole of peroxide. ^b In moles of CO₂ or carboxyl groups/mole of peroxide. ^c In moles of radicals incorporated/mole of peroxide. ^d As tetrahydroquaterphenyl. ^e Total value.

compare these absorptions with exact structural analogues. However, acyl carbonates have absorptions around 1800 and 1740 cm⁻¹,⁹ and the modification of this structure to form 2 is expected to shift the carbonyl absorptions toward higher frequency. Thus, these two IR bands are consistent with structure 2. The ¹H NMR of the ozonolysis product in CDCl₃ reveals that all of the hydrogens are bound to aromatic rings. Importantly, the ¹H NMR shows two sets of doublets (four protons) at 8.02–8.12 ppm and a multiplet (six protons) at 7.35–7.70 ppm. The presence of the downfield doublets is indicative of benzoyl groups, and the fact that there are two doublets confirms that the benzoyl groups are nonequivalent. The ¹³C NMR of the ozonolysis product in CDCl₃ shows 11 lines, three of which are in the carbonyl region (162, 158.9, and 146.9 ppm). The remaining lines are in the aromatic region (124.6–135.2 ppm). The lines at 162.0 and 158.9 ppm indicate nonequivalent benzoyloxy groups, and the line at 146.9 ppm is consistent with a carbonate carbonyl group.

Final conformation of the assigned structure for the ozonolysis product comes from its reaction with trimethyl phosphite. This reduction gives benzoic anhydride in 69% isolated yield.¹⁰



Thermolysis of 2. The thermolysis of monoperoxy-carbonate 2 in benzene gives benzoic acid, biphenyl, phenyl benzoate, and CO₂. In addition, there is a neutral, non-volatile residue that we assign as tetrahydroquaterphenyl.⁵ The product yields are detailed in Table I. Basically, we can account, within experimental error, for all of the fragments of 2 among the products we detect.

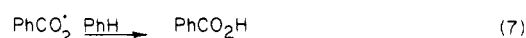
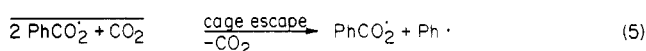
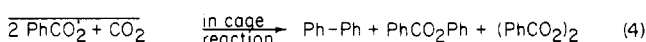
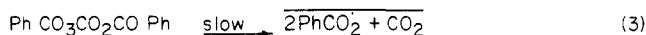
The thermal decomposition of a 2.23 × 10⁻² M solution of 2 in benzene exhibits first-order kinetics over the temperature range we examined (60.1–81.1 °C). This observation, and the experiments carried out in the presence of the stable free radical galvinoxyl described below, rule out radical-induced homolysis reactions under these conditions. Examination of the temperature dependence of the rate for the unimolecular thermolysis of 2 (Table II) reveals that Δ*H*[‡] = 27.8 ± 1.2 kcal/mol and that Δ*S*[‡] = 6.1 ± 3.5 eu. The entropy of activation, in particular, is consistent with an uncatalyzed unimolecular reaction, as is the relatively low value for the enthalpy of activation.¹¹

When the decomposition of 2 is carried out in the presence of galvinoxyl at 79.3 °C, the rate constant of reaction is (1.22 ± 0.01) × 10⁻³ s⁻¹. The absence of a sig-

Table II. Rate Constants for Thermolysis in Benzene

temp, °C	10 ⁵ <i>k</i> ₁ , s ⁻¹	temp, °C	10 ⁵ <i>k</i> ₁ , s ⁻¹
60.00	8.05 ± 0.55	74.90	49.5 ± 2.5
66.02	19.2 ± 0.6	81.10	111 ± 2
70.10	26.3 ± 2.5		

Scheme I



nificant inhibition of rate of the reaction of 2 with galvinoxyl in the solution is inconsistent with a measurable induced decomposition path. Indeed, the slight acceleration of the reaction rate in the presence of galvinoxyl may signal the operation of an electron transfer induced reaction. We have observed similar electron-transfer processes in the reaction of galvinoxyl and other peroxides and are continuing to examine this path.¹² Quantitative determination of the amount of galvinoxyl consumed during the thermolysis of 2 was accomplished by spectrophotometry. These measurements show that at most 60% of the peroxy-carbonate 2 that reacts under these conditions gives cage-escaped radicals. Consistent with this notion is the observation that the yield of biphenyl drops from 64 to 22% in the presence of galvinoxyl at 79.8 °C. Thus, biphenyl must be a product of both in-cage and cage-escaped radicals. On the other hand, the yield of phenyl benzoate increases from ca. 6 to 20% when galvinoxyl is added to the reaction mixture. This change is consistent also with the partial intervention of an electron-transfer path in the presence of galvinoxyl.

We investigated briefly the effect of solvent polarity on the thermolysis of 2. The rate constant for reaction of 2 in CH₃CN at 79.8 °C is (9.64 ± 1) × 10⁻⁴ s⁻¹, not significantly different from the benzene solvent value. Thus, we conclude that the carboxy inversion reaction, which is typically accelerated by polar solvents,¹³ does not contribute to the reaction of 2.

The thermolysis of peroxy-carbonate 2 in benzene gives products quite similar to those obtained from the thermolysis of benzoyl peroxide. The formation of these products, and the observed kinetic behavior, can be understood in terms of the reactions in Scheme I. Several points concerning Scheme I warrant further discussion. The relatively low Δ*S*[‡] for reaction 3 is consistent with the direct expulsion of CO₂, simultaneously forming two benzoyloxy radicals.¹¹ Viewed in its simplest form, this reaction generates these radicals separated initially by a CO₂ molecule. The ratio of cage escape (eq 4) to cage recombination (eq 5) deduced from the galvinoxyl trapping experiment indicates that, despite the presence of the CO₂, cage recombination in this case is significantly more efficient than for the case of benzoyl peroxide (89% cage escape).¹⁴ This is contrary to the results of Kiefer and Taylor⁸ and may indicate considerable motion within the

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(14) A reinterpretation of results from ref 7: *k*₁(scavenged)/*k*₁(not scavenged) = 1.67 × 10⁻⁵/1.88 × 10⁻⁵ = 89%.¹⁸

cage before recombination or escape occurs.

In eq 4 we indicate the possible formation of benzoyl peroxide as an in-cage product of the thermolysis of **2**. Indeed, direct thermolysis of benzoyl peroxide does produce some in-cage regeneration of the reactant.¹⁵ However, we are not able to detect any benzoyl peroxide, either spectroscopically or kinetically, during the reaction of **2**. Computer simulation of the reaction kinetics indicates that we would be unable to detect less than 5% of this product.

In summary, the ozonation of diphenylvinylene carbonate gives dibenzoyl monoperoxycarbonate, the first reported compound of its class. Its formation is consistent with the Criegee mechanism for the ozonation of olefins. The thermolysis of dibenzoyl monoperoxycarbonate produces the same radicals as benzoyl peroxide, but at a significantly greater rate. This might make **2** useful as a source of free radicals.

Experimental Section

General Methods. IR spectra were recorded on a Perkin-Elmer 237B or a Perkin-Elmer 137 instrument. The ¹H NMR spectrum was determined on a Varian HR-220 instrument using an internal deuterium lock. The ¹³C NMR spectrum was measured on a Varian XL-100, also with an internal deuterium lock. The acquisition time was 1.35 s, and 56 000 transients were averaged. Visible absorptions were recorded with a Perkin-Elmer 101 instrument. Temperatures were measured with a NBS thermometer. The ozonation was done with a Welsbach ozonizer. Microanalysis was performed by J. Nemeth and associates, University of Illinois. Diphenylvinylene carbonate (**1**) was prepared by the method of Lewis and Hirsh.¹⁶

Dibenzoyl Monoperoxycarbonate (2). Diphenylvinylene carbonate (1.00 g, 4.20 mmol) was dissolved in 50 mL of CH₂Cl₂ and cooled in an ice bath. Ozone (9 mmol, 3 mol % in O₂) was bubbled in through a glass frit. After ozonation, the solvent was removed in vacuo, and the resulting solid was recrystallized from hexane, giving 0.908 g (3.17 mmol) of dibenzoyl monoperoxycarbonate (75.6%): mp 87 °C; ¹H NMR (220 MHz, CDCl₃) δ 8.10 (d), 8.03 (d), 7.70–7.35 (m); ¹³C NMR (25.2 MHz, CDCl₃) δ 162.1, 158.9, 146.9, 135.2–124.6 (8 lines); IR (CCl₄) 1853, 1787 cm⁻¹. Anal. Calcd for C₁₅H₁₀O₆: C, 62.94; H, 3.52; active O, 5.59. Found: C, 63.02; H, 3.62; active O, 5.57.

Thermolysis of 2 in Benzene. The products and yields were determined as follows. A 0.1278-g (0.447 mmol) sample of **2** was dissolved in 20 mL of benzene and heated at reflux for 2 h. A small flow of N₂ was maintained at all times, and the escaping gasses were passed through two dry ice/alcohol traps to remove solvent vapors and then into an ascarite trap. The ascarite gained 0.0404 g, which corresponds to 0.918 mmol of CO₂ (yield 2.05 mol/mol of peroxide). After the reaction mixture was cooled, 0.0800 g of phenanthrene was added to the reaction mixture as

an internal standard, and comparison by GLC [6-ft column, SE-30 (4%), 200 °C] to a standard solution gave biphenyl (0.0442 g, 0.287 mmol, 0.642 mol/mol of peroxide) and phenyl benzoate (0.00455 g, 0.023 mmol, 0.051 mol/mol of peroxide). The solvent was then removed in vacuo, and the white solid which resulted was dried for 2 h in vacuo. The mass of the residue was 0.242 g. This was dissolved in 20 mL of 2-propanol and titrated to a phenolphthalein end point with 6.18 mL of NaOH (0.0503 N). This corresponds to 0.311 mmol of benzoic acid. An extraction with NaOH of another sample had shown the acidic product to be benzoic acid. The residue not accounted for by biphenyl, phenyl benzoate, benzoic acid, and phenanthrene corresponds to 0.24 mmol when taken as tetrahydroquaterphenyl.

The rate constants for the thermal decomposition of **2** in benzene were determined as follows. A 0.1274-g sample of **2** was placed in a sealed tube with 20 mL of benzene, and the tube was placed in a thermostated water bath. For samples at 60.00, 70.10, and 91.10 °C, the method of Banerjee and Budke¹⁷ was used. Samples were taken at appropriate time intervals over 2 half-lives, and a 1-mL aliquot was diluted to 25 mL with a 2:1 mixture of acetic acid and CHCl₃ and then purged with N₂ for 1 min. Finally, 1 mL of 50% KI was then added, and the visible absorbance of the triiodide formed was measured at 470 nm. For the samples at 66.02 and 75.90 °C, the relative peroxide concentrations were determined by IR. A plot of the absorbance of the peak at 1787 cm⁻¹ for known concentrations of the peroxide against concentration was shown to be linear. Semilogarithmic plots of the absorbances determined by the above methods were made, and least-squares analyses gave the rate constants and deviations listed in Table II.

Thermolysis of 2 in the Presence of Galvinoxyl. Galvinoxyl was obtained from Aldrich Chemical Co. and was shown to be pure by iodometric titration.¹⁸ For the kinetic analysis, 6.81 mg (0.0238 mmol) of **2** and 18.98 mg (0.045 mmol) of galvinoxyl were dissolved in 25 mL of benzene. The visible absorbance of the galvinoxyl at 733 nm in this mixture was measured continuously. Importantly, galvinoxyl was shown not to decompose spontaneously under these conditions.

To determine the fraction of cage escape, we diluted 0.02014 g (0.0477 mmol) of galvinoxyl and 0.0594 g (0.0208 mmol) of **2** to 25 mL with benzene and purged the mixture with N₂ for 5 min. The absorbance of this solution was measured at 740 nm. Samples were then placed in three tubes, purged for an additional minute, and sealed. After reaction for 1.5 h at 97.90 °C, the absorbances were again measured, and the amount of galvinoxyl consumed was determined.

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Registry No. **1**, 21240-34-6; **2**, 72611-68-8; ozone, 10028-15-6.

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