stirrer was placed 22.4 g (0.05 mol) of salt **20**, 14.4 g (0.10 mol) of sodium salicyloxide, and 150 ml of dry DMF, and the mixture was stirred at reflux for 2 days. It was worked up by pouring into water, acidifying, and extracting with ether. The dry ($MgSO_4$) organic extract was short path distilled; volatiles showed only solvents and salicylaldehyde. The distillation residue was column chromatographed to furnish 6.0 g (50% yield) of **19** and 9.3 g (67%) of triphenylphosphine oxide (**7a**).

Reaction of Salt 4 with the Sodium Salt of Pyrrolaldehyde.—To a flask containing 150 ml of dry ether and 3.16 g (0.075 mol) of 57% sodium hydride dispersion (Alfa) was added 7.15 g (0.075 mol) of pyrrolaldehyde. When hydrogen evolution had ceased (*ca.* 2 hr), 33.4 g (0.075 mol) of salt **4** was added and the mixture was refluxed for 10 hr. DMF (50 ml) was added, and the red-brown mixture was refluxed for an additional 12 hr. After cooling, the reaction mixture was poured into dilute aqueous acid and filtered, providing 18.2 g of purple solid **21**. The filtrate was extracted with ether and dried ($MgSO_4$). Evaporation of the ether left a mixture of **7a** and **21**, from which 12.5 g (60% yield) of triphenylphosphine oxide (**7a**) could be isolated by digestion with hot hexane. Compound **21** was dissolved in $CHCl_3$ and reprecipitated into ether for analysis, mp >300°.

Anal. Calcd for $C_{143}H_{126}BrN_{10}OP$, $n = 9$: C, 81.87; H, 5.95; N, 6.45. Found: C, 81.46; H, 6.07; N, 6.72.

Polymer **21** had ir (Nujol) 1600 (C=C), 920 (pyrrole), 760, 700 cm^{-1} (aromatic and pyrrole ring); nmr ($CDCl_3$) showed broad adsorptions at δ 1.8–4.2, 4.5–5.0, 5.8–6.3, 6.8–7.5; uv $\lambda_{max}^{CHCl_3}$ 242, 280, 350, 500 mμ; mol wt (osmometry) calcd 2171, found 2180.

Reaction of 4 with the Sodium Salt of Phenylbenzoin.—The sodium salt of phenylbenzoin was prepared by treating 8.65 g (0.03 mol) of phenylbenzoin dissolved in 100 ml of dry ether with 1.44 g (0.03 mol) of a 50% dispersion of sodium hydride. After stirring for 15 min, 13.4 g (0.03 mol) of salt **4**, dissolved in 100 ml of DMF, was added and the resultant mixture was stirred at ambient temperature for 2 days, then heated for 6 hr at 100°. The mixture was poured into water and extracted with ether. Chromatography of the dry ($MgSO_4$) ether extract on silica gel yielded (in order of elution) **22**, 4.1 g (47.5%); **8d**, 1.7 g (15%); **7a**, 4.4 g (52.8%).

2,2,3,4-Tetraphenyl-2,5-dihydrofuran (8d) had mp 109–110° (MeOH); ir (KBr) 1650, 1590 (C=C), 1480, 1330 (CC), 1230 (COC), 790, 770, 750, 690 cm^{-1} (aromatic); nmr ($CDCl_3$) δ 3.85 (s, 2, CH_2), 6.8–7.9 (m, 20, C_6H_5); uv $\lambda_{max}^{CHCl_3}$ 242 mμ (ϵ 10,000), 312 (9400).

Anal. Calcd: C, 89.78; H, 5.92. Found: C, 90.19; H, 6.11.

Rearrangement of the Sodium Salt of Phenylbenzoin.—A 5.76-g (0.02 mol) sample of phenylbenzoin in 100 ml of dry ether was treated with 0.96 g (0.02 mol) of a 50% dispersion of sodium hydride. When hydrogen evolution had ceased, 75 ml of dry DMF was added, and the mixture was heated at reflux for 2 hr, then stirred at room temperature for 24 hr. The mixture was poured into water and dilute acid was added until neutrality was reached. Extraction with ether resulted in the isolation of 4.7 g (81% yield) of benzhydryl benzoate (**22**), identical with an authentic sample. Hydrolysis in dilute acid furnished benzoic acid and benzhydrol (70% based on phenylbenzoin), identified by comparison of ir and nmr spectra and mixture melting point with authentic samples.

Registry No.—**2**, 30670-21-4; **3**, 7301-95-3; **4**, 30537-11-2; (*Z*)-**5b**, 38555-27-0; (*E*)-**5b**, 38555-28-1; **5c**, 38555-29-2; **6** (R′ = Me), 38555-30-5; **8** (R′ = Me), 38555-31-6; **8d**, 38555-32-7; **9** (R′ = Me), 38555-33-8; **10**, 38555-34-9; **10** bromide derivative, 33999-09-6; **19**, 38555-36-1; **20**, 30537-09-8; **21**, 38555-38-3; 2-bromopropene, 557-93-7.

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The Preparation, Thermolysis, and Photolysis of Phenylmaleoyl Peroxide

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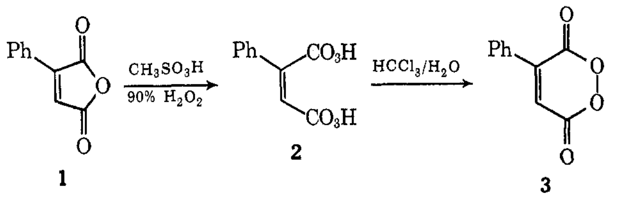
The decomposition of the cyclic monomeric peroxide derived from phenylmaleic acid generates carbon dioxide, phenylacetylene, and a carbonyl-containing polymeric substance. The yields of carbon dioxide and phenylacetylene are highest in a sensitized photolytic decomposition, and lowest in a thermolytic decomposition. These results are interpreted in terms of the nature of the likely intermediates in the decomposition sequence.

The chemistry of cyclic acyl peroxides has attracted the interest of organic chemists sporadically for many years. Phthaloyl peroxide was the first cyclic acyl peroxide to be investigated thoroughly.[1–5] More recently, cyclic malonyl peroxides have been the subject of several studies.[6,7] Cyclic acyl peroxides have also been implicated in the decomposition of dimeric and trimeric peroxides of cycloalkanones.[8] Cyclic diphenoyl peroxide has been prepared, but its chemistry has not been extensively explored.[9]

In this report, we wish to describe the synthesis, thermolysis and photolysis of phenylmaleoyl peroxide, **3**. This compound is the first monomeric cyclic maleoyl peroxide to be reported.

Results and Discussion

Synthesis.—Phenylmaleoyl peroxide (**3**) was generated in 38% yield when a heterogeneous mixture consisting of diperoxyphenylmaleic acid, **2**, chloroform, and water was agitated vigorously. The success of this procedure depends upon the rapid cyclization of **2** to **3** in the polar aqueous phase, following which the less polar **3** is rapidly extracted into the inert chloroform phase, thereby preventing further hydrolysis to the monoperoxy acid.



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[1] K. E. Russell, *J. Amer. Chem. Soc.*, **77**, 4814 (1955).

[2] F. D. Greene, *ibid.*, **78**, 2246 (1956).

[3] G. Wittig and H. F. Ebel, *Justus Liebigs Ann. Chem.*, **650**, 20 (1961).

[4] M. Jones, Jr., and M. R. DeCamp, *J. Org. Chem.*, **36**, 1536 (1971).

[5] V. Dvorak, J. Kolc, and J. Michl, *Tetrahedron Lett.*, 3443 (1972).

[6] W. Adam and R. Rucktäschel, *J. Amer. Chem. Soc.*, **93**, 557 (1971).

[7] O. L. Chapman, P. W. Wojtkowski, W. Adam, O. Rodriquez, and R. Rucktäschel, *ibid.*, **94**, 1365 (1972).

[8] P. R. Story, D. D. Denson, C. E. Bishop, B. C. Clark, Jr., and J. C. Farine, *ibid.*, **90**, 817 (1968).

[9] F. Ramirez, S. B. Bhatia, R. B. Mitra, Z. Hamlet, and N. B. Desai, *ibid.*, **86**, 4394 (1964).

Decompositions.—The decomposition of **3** proceeds smoothly under conditions of thermolysis, direct photolysis, and photolysis in the presence of a triplet sensitizer. Three products, carbon dioxide, phenylacetylene and a carbonyl-containing polymer which was not fully characterized, together account for all of the peroxide decomposed. The relative yields of these three substances are dependent upon the mode of decomposition.

$$\mathbf{3} \longrightarrow CO_2 + PhC{\equiv}CH + \text{polymer}$$

The yields of carbon dioxide and phenylacetylene are summarized in Table I. Clearly, the yields of these two products are higher in a photolysis than in a thermolysis, and higher when the photolysis is sensitized than when it is not.

TABLE I

YIELDS OF CARBON DIOXIDE AND PHENYLACETYLENE FROM THE DECOMPOSITION OF PHENYLMALEOYL PEROXIDE

	Yield, mol/mol 3	
Conditions	CO_2	PhC_2H
Thermolysis (refluxing CCl_4)	1.10	0.13
Direct photolysis (CCl_4, 22-25°)	1.62	0.63
Sensitized photolysis (CCl_4, 22-25°, benzil)	1.88	0.82

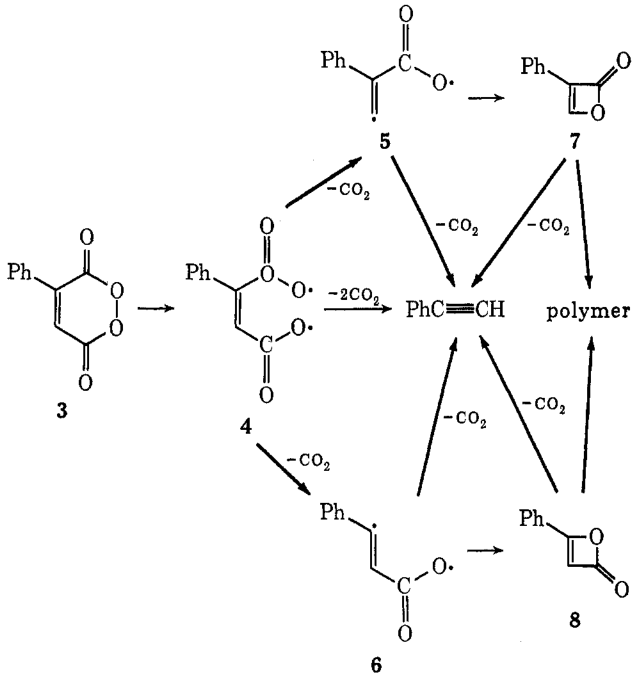
Before advancing an interpretation of these findings based upon the properties of the expected intermediates, it is necessary to consider the possible intervention of a side reaction which would influence these product yields. Phthaloyl peroxide is known to add to acetylenes by a nondecarboxylative process.[10] If an analogous reaction were to occur between **3** and the phenylacetylene being produced during the decomposition, the yields of both carbon dioxide and phenylacetylene would be affected. To test for the possible intervention of this reaction, the thermolysis of **3** was carried out in the presence of several equivalents of added phenylacetylene. If the addition of **3** to phenylacetylene occurs with sufficient facility to compete with the decomposition of **3**, it would be expected that the yield of carbon dioxide would be significantly below the yield obtained in the absence of added phenylacetylene. In fact, in the presence of 2 equiv of phenylacetylene, 1.04 equiv of carbon dioxide was evolved, an amount only slightly less than the value of 1.10 obtained in the absence of added phenylacetylene. Thus, it can be concluded that a competing reaction between **3** and phenylacetylene formed during the decomposition is not occurring to any significant extent.

Although additional studies will be required to establish rigorously the mechanism for the decomposition of phenylmaleoyl peroxide, the results obtained herein may be discussed within the framework of Scheme I.

Thermolysis of the oxygen–oxygen bond of **3** would generate a short-lived diacyloxy radical **4**, which could produce phenylacetylene directly, or *via* the monoacyloxy diradicals **5** and **6** formed by monodecarboxylation of **4**, or from unstable lactonic intermediates such as **7** and **8**. Polymeric materials could also arise from **7** and **8**, or from ketene intermediates derived from **7** and **8** by a process analogous to one observed in the decomposition of phthaloyl peroxide.[5]

SCHEME I

THE DECOMPOSITION OF PHENYLMALEOYL PEROXIDE



The photosensitized decomposition of **3** must be interpreted in terms of triplet states of the intermediates. If the monoacyloxy diradicals **5** and **6** are triplets, spin inversion would be required before nonradical species **7** and **8** could be formed. The sequence leading to polymer would thereby be disfavored relative to the competing decarboxylation reaction, which would produce phenylacetylene. The possibility of a photosensitized decarboxylation of nonradical intermediates **7** and **8** to phenylacetylene cannot be excluded.

The results of the direct photolysis of **3** can be interpreted in several ways. The relatively high yields of carbon dioxide and phenylacetylene may suggest that the direct photolysis is also occurring primarily *via* triplet intermediates. On the other hand, direct photolysis may generate singlet intermediates similar to those produced during thermolysis, in which case the higher yields of phenylacetylene and carbon dioxide observed during photolysis may reflect a different partition of the intermediates **7** and **8** between decarboxylation and polymerization at the lower temperature of the photolysis (25° *vs.* 76°). Or, direct photolysis might produce higher energy singlet species **5** and **6** than thermolysis. Higher energy singlet intermediates might be more prone to decarboxylation than cyclization. Finally, photolytic decarboxylation of the nonradical intermediates **7** and **8** may account for the higher yields of carbon dioxide and phenylacetylete under photolytic than thermolytic conditions.

Experimental Section

Caution. Although we experienced no problems in handling any of the materials described in this paper, we urge that all of these peroxidic compounds be treated as potentially hazardous substances.

Diperoxyphenylmaleic Acid (2).—Phenylmaleic anhydride,[11,12] methanesulfonic acid, and 90% hydrogen peroxide in molar ra-

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[10] F. D. Greene and W. W. Rees, *J. Amer. Chem. Soc.*, **82**, 893 (1960).

[11] L. E. Miller, H. B. Staley, and D. J. Mann, *ibid.*, **71**, 374 (1949).

[12] C. S. Rondesvedt and A. H. Filbey, *J. Org. Chem.*, **19**, 119 (1954).

tios of 1:5:6 were stirred at room temperature for 90 min. An equal volume of cold, saturated ammonium sulfate solution was added, and the mixture was extracted four times with equal volumes of ether. The ether solution was washed twice with cold, saturated ammonium sulfate, dried over magnesium sulfate, filtered, and concentrated at reduced pressure and room temperature, leaving a viscous oil. Crystallization was induced by adding sufficient chloroform, containing a little ether, to produce a clear solution, then removing solvent at reduced pressure. The solid obtained was triturated with several portions of chloroform and dried *in vacuo* to give a 57% yield of crude diperoxy acid containing greater than 98% of the theoretical active oxygen. Recrystallization from chloroform–ether gave pure diperoxyphenylmaleic acid: mp 92.5–93.5°; ir (Nujol) 3270, 1760, 1625, 1600, 1580, 680 cm^{-1}.

Anal. Calcd for $C_{10}H_8O_6$: C, 53.58; H, 3.60; active oxygen,[13] 14.27. Found: C, 53.43; H, 3.59; active oxygen, 14.00.

Phenylmaleoyl Peroxide (3).—A mixture of diperoxyphenylmaleic acid (0.50 g, 2.1 mmol) of 96% purity, 5 ml of water, and 50 ml of chloroform was agitated at room temperature for 60 min with a Vibromixer. The aqueous phase was washed with 5 ml of chloroform, and the combined chloroform layers were washed twice with 5 ml of cold, 10% sodium bicarbonate, dried over magnesium sulfate, filtered, and evaporated, giving a 38% yield of phenylmaleoyl peroxide of 94–96% purity. One recrystallization from chloroform–hexane gave 0.13 g (33%) of pure product: mp 105.5–106°; ir ($HCCl_3$) 3070, 4040, 1765 (shoulder), 1750, 1630, 1605, 1580, 700 cm^{-1}; uv (CCl_4) broad λ_{max} 312 nm (log ϵ 4.06); nmr ($CDCl_3$) δ 7.23 (s, 1 H), 7.3–7.9 (b m, 5 H). Phenylmaleoyl peroxide is very soluble in methylene chloride and chloroform, soluble in benzene, slightly soluble in carbon tetrachloride, and practically insoluble in hexane.

Anal. Calcd for $C_{10}H_6O_4$: C, 63.16; H, 3.18; active oxygen, 8.41; mol wt, 190.15. Found: C, 63.25; H, 3.21; active oxygen, 8.25; mol wt, 190 (cryoscopic, benzene).

Hydrolysis of phenylmaleoyl peroxide in aqueous acetone, followed by dehydration with trifluoroacetic anhydride, gave phenylmaleic anhydride, mp 117–119° (lit.[11] mp 119–120°).

Decomposition Studies.—A 0.02–0.1 *M* solution of phenylmaleoyl peroxide in carbon tetrachloride was placed in a flask equipped with a reflux condenser. A stream of dried, prepurified nitrogen was passed into the reaction flask through a tube which ended a few centimeters above the surface of the refluxing solvent for the thermal decompositions, or through a fritted gas dispersion tube submerged in the medium for the photodecompositions. The nitrogen stream leaving the top of the reflux condenser was passed through a trap cooled in Dry Ice–acetone, then two U tubes filled with Ascarite, and finally through a bubbler containing sulfuric acid. The weight of carbon dioxide evolved was obtained from the increase in weight of the first Ascarite U tube.

In a typical thermal decomposition, the system was flushed with nitrogen at room temperature until the first Ascarite U tube came to constant weight. The reaction flask was then immersed in an oil bath 5–10° above the boiling point of the solvent while the nitrogen continued to flow. At intervals, the flow was stopped, and the first Ascarite U tube was removed and weighed. Refluxing was continued until the Ascarite trap came to constant weight.

In a typical photodecomposition, the Pyrex reaction flask was immersed in a bath maintained at 22–25°. The system was flushed with nitrogen and a constant weight for the first Ascarite tube was obtained. The reaction mixture was then irradiated with a 275-W sun lamp mounted over the reaction flask at a distance of 4 in. until the Ascarite U tube reached constant weight.

The direct photolysis of 40 mg of phenylmaleoyl peroxide in 12 ml of carbon tetrachloride was 80% complete in 5 hr. In the presence of 8 mg of benzophenone, 98% decomposition occurred in 5 hr. In the presence of 80 mg of benzophenone decomposition was 90% complete in 2 hr, 99% in 4 hr. Finally, in the presence of 40 mg of benzil, decomposition was 99% complete in 2 hr. In the absence of light no decomposition was observed over 10–12 hr in the presence or absence of sensitizer.

The yield of phenylacetylene was obtained by diluting the reaction mixture to 100 ml and determining the concentration of phenylacetylene by glc on a silicone gum rubber column, using solutions of phenylacetylene of known concentration as reference standards.

At the completion of thermolysis, the reaction mixture contained a floating precipitate. The mixture was concentrated to about one-fourth its original volume, and the precipitate was filtered, washed with a little carbon tetrachloride, and dried, giving a yellow powder amounting to about 50% of the weight of initial peroxide. This substance exhibited a broad absorption band between 1800 and 1670 cm^{-1}. The average molecular weight (vapor pressure osmometry in chloroform) was 3400. The filtrate obtained after removal of the insoluble material was then distilled at reduced pressure until all solvent and phenylacetylene had been removed. The residue consisted of a brown, sticky solid amounting to about 25% of the weight of the initial peroxide. This material exhibited broad absorption between 1860 and 1675 cm^{-1}, and had an average molecular weight of 435.

Photolytic decompositions produced only the soluble residues. No insoluble polymer was generated. Yields of residues were determined simply by weighing the material remaining after solvent and phenylacetylene had been removed by distillation. In the case of the sensitized decompositions, the weight of sensitizer had to be subtracted from the observed weight of the residue.

In all cases the residue was examined by glc on a silicone column for the presence of hexachloroethane. None was ever detected.

Registry No.—**1**, 36122-35-7; **2**, 38605-60-6; **3**, 38606-11-0.

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[13] (a) L. S. Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958); (b) *J. Amer. Chem. Soc.*, **81**, 2364 (1959).