

TABLE I
 1,3-DICHLOROTETRAFLUOROACETONE CYANOHYDRIN ESTERS

Reagent used	Ester (ClCF ₂) ₂ C<	OR CN	M.p. or b.p. (mm.), °C.	% yield
<i>p</i> -Nitrobenzoyl chloride	<i>p</i> -Nitrobenzoate		112–113	65
<i>p</i> -Nitrobenzenesulfonyl chloride	<i>p</i> -Nitrobenzenesulfonate		105–107	94
Trifluoroacetic anhydride	Trifluoroacetate		31 (23)	30 crude, 19 pure
Phosphorus trichloride	Tris(1,3-dichlorotetrafluoroisopropyl) phosphite		53–55 (0.1)	15
Phosphorus pentachloride	1,3-Dichlorotetrafluoroisopropyl tetrachlorophosphate		115 (25)	28

afforded thionyl fluoride, and, while some gas was evolved in this reaction, no evidence was adduced for the presence of thionyl fluoride. A careful search for volatile fragments was made in each case, using gas chromatography, and none was detected.

Experimental

1,3-Dichlorotetrafluoroacetone Cyanohydrin Sodium Salt.—In a 250-ml. three-necked flask, fitted with stirrer and dropping funnel, were placed 100 ml. of tetrahydrofuran and 4.9 g. (0.10 mole) of sodium cyanide. 1,3-Dichlorotetrafluoroacetone (20 g., 0.10 mole) was added dropwise to the stirred, cold (5°) suspension. The sodium cyanide dissolved within 1 hr., giving an orange solution. Evaporation of the solution at the water pump, followed by trituration with ether, afforded 19.5 g. of white powder (79% yield).

Anal. Calcd. for C₄Cl₂F₄NNaO (248): N, 5.65; Na, 9.32. Found: N, 6.03, 5.76; Na, 9.49.

Similar experiments using perfluoroacetone, 1,1,3-trichlorotrifluoroacetone, and 1,1,3,3-tetrachlorodifluoroacetone afforded 87, 49, and 32% yields, respectively, of the cyanohydrin sodium salts of these ketones. Potassium cyanide was found to react more readily with all of the ketones but gave lower yields in tetrahydrofuran than did sodium cyanide. A suspension of potassium cyanide in ether containing 5 vol. % of tetrahydrofuran reacted rapidly and cleanly with all of the ketones, giving white slurries of the potassium salts.

1,3-Dichlorotetrafluoroacetone Cyanohydrin *p*-Nitrobenzoate.—A solution of 4.8 g. (0.026 mole) of *p*-nitrobenzoyl chloride in 10 ml. of dry tetrahydrofuran was added to a stirred solution of 6.5 g. (0.026 mole) of the cyanohydrin sodium salt in 50 ml. of dry tetrahydrofuran at 0°. The mixture was heated at 50° for 3 hr. and the solvent was removed at the water pump. The residue was triturated with 100 ml. of boiling heptane. The suspension was filtered hot and the filtrate was cooled in ice and filtered to give 7.5 g. (65% yield) of the benzoate ester, m.p. 112–113°, $\lambda_{\text{max}}^{\text{CCl}_4}$ 5.60 μ . A sample was recrystallized in good yield from heptane: m.p. 112–113°.

Anal. Calcd. for C₁₁H₄Cl₂F₄N₂O₄ (375.1): C, 35.2; H, 1.08; Cl, 18.9. Found: C, 35.4; H, 1.43; Cl, 18.8.

1,3-Dichlorotetrafluoroacetone Cyanohydrin *p*-Nitrobenzenesulfonate Ester.—*p*-Nitrobenzenesulfonyl chloride (45 g., 0.20 mole) (Eastman White Label) in 60 ml. of THF was added dropwise to 0.20 mole of the cyanohydrin sodium salt in 100 ml. of THF. The mixture was heated to 50° for 3 hr., then evaporated on the steam bath. The crystalline residue was dissolved in hot heptane–benzene (1:1) and filtered. A total of 61 g. (74% yield) of sulfonate ester was obtained in two crops (47 and 14 g.): m.p. 106–108°; $\lambda_{\text{max}}^{\text{CCl}_4}$ 6.5, 7.1, and 8.3 μ .

Anal. Calcd. for C₁₀H₄Cl₂F₄N₂O₅S (411): C, 29.2; H, 0.975; Cl, 17.5; N, 6.83; S, 7.74. Found: C, 29.4; H, 1.20; Cl, 16.8; N, 6.85; S, 7.37.

1,3-Dichlorotetrafluoroacetone Cyanohydrin Trifluoroacetate Ester.—Distilled trifluoroacetic anhydride (21 g., 0.10 mole) was added slowly to a chilled, fine suspension of 0.10 mole of cyanohydrin sodium salt in 50 ml. of ether. The mixture was refluxed 1 hr., distilled on a 15-in. spinning-band column at 1 atm. to remove ether, and then distilled at 45 mm. to give 8.7 g. of a mixture of the desired ester (5.4 μ) and trifluoroacetic acid (5.6 μ). Careful redistillation at 23 mm. gave five fractions containing decreasing amounts of free acid. The last two fractions (very moisture sensitive) were taken for characterization: 4.19 g. (13%); b.p. 30.5–31° (23 mm.); $\lambda_{\text{max}}^{\text{neat}}$ 5.43, 7.52, and 8–9 μ .

Anal. Calcd. for C₆Cl₂F₇NO₂ (323): C, 22.4; Cl, 22.0; N, 4.34. Found: C, 23.1; Cl, 20.0; N, 4.02.

Tris(1,3-dichlorotetrafluoroisopropyl) Phosphite.—A mixture of 9.4 g. (0.066 mole) of distilled phosphorus trichloride and 49.8 g. (0.20 mole) of cyanohydrin sodium salt in 100 ml. of THF was stirred at 25° for 40 hr., then filtered. The filtrate was stripped of solvent at the water pump, then distilled through a 15-in. spinning-band column. A fraction boiling at 95° (1 mm.) was taken: 7.3 g. (15%); $\lambda_{\text{max}}^{\text{CCl}_4}$ 6.0, 7.8, and 8.5–9.5 μ .

Anal. Calcd. for C₁₂Cl₆F₁₂N₃O₃P (706): C, 20.4; Cl, 30.2; N, 5.95; P, 4.33. Found: C, 20.0; Cl, 31.0; N, 5.81; P, 4.09.

Bis(1,3-dichlorotetrafluoroisopropyl) Sulfite.—A mixture of 11.9 g. (0.10 mole) of thionyl chloride and 24.9 g. (0.10 mole) of cyanohydrin sodium salt in 60 ml. of THF was stirred at 25° for 15 hr. After removal of solvent at the water pump, the residual liquid was filtered from the sodium chloride using ether solvent. Distillation of the mixture, ultimately at ca. 0.01 mm., gave 4.19 g. (19%) of a fuming liquid: b.p. 51–53° (0.01 mm.); $\lambda_{\text{max}}^{\text{CCl}_4}$ 6.0, 7.7, and 8–9.5 μ .

Anal. Calcd. for C₈Cl₄F₈N₂O₃S (498): C, 19.3; Cl, 28.5; N, 5.62; S, 6.44. Found: C, 19.5; H, 0.3; Cl, 28.5; N, 5.66; S, 6.54.

1,3-Dichlorotetrafluoroisopropyl Tetrachlorophosphate.—1,3-Dichlorotetrafluoroacetone cyanohydrin was prepared *in situ* by vigorously stirring 10 g. (0.050 mole) of dichlorotetrafluoroacetone with 2.45 g. (0.050 mole) of dry sodium cyanide in 50 ml. of ether containing 5 ml. of THF. A bulky precipitate of the cyanohydrin sodium salt formed, replacing the granular sodium cyanide after 12–15 hr. at 25°. Anhydrous hydrogen chloride was bubbled through the mixture until an excess was present (*Caution, use hood*). The mixture was filtered, stripped of solvent at the water pump, then heated with 11 g. (0.053 mole) of phosphorus pentachloride for 3 hr. at 100°. A clear, colorless liquid formed. Distillation gave a colorless, viscous, fuming liquid: 5.2 g. (28%); b.p. 114–115° (14 mm.); $\lambda_{\text{max}}^{\text{CCl}_4}$ 6.45, 6.9, and 7.8 μ .

Anal. Calcd. for C₄Cl₆F₄NOP (398): C, 12.05; Cl, 51.4; N, 3.52; P, 7.79. Found: C, 13.1; Cl, 52.5; N, 3.38; P, 7.84.

Electron Paramagnetic Resonance Studies of Homolytic Carbon–Oxygen and Oxygen–Oxygen Fission in Symmetrical Biscyclohexadien-4-one Peroxides

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Received July 20, 1964

Evidence has been presented that (a)¹ bis(1-phenyl-3,5-di-*t*-butyl-2,5-cyclohexadien-4-one) peroxide (I) and (b)^{2,3} bis(1,3,5-tri-*t*-butyl-2,5-cyclohexadien-4-one) per-

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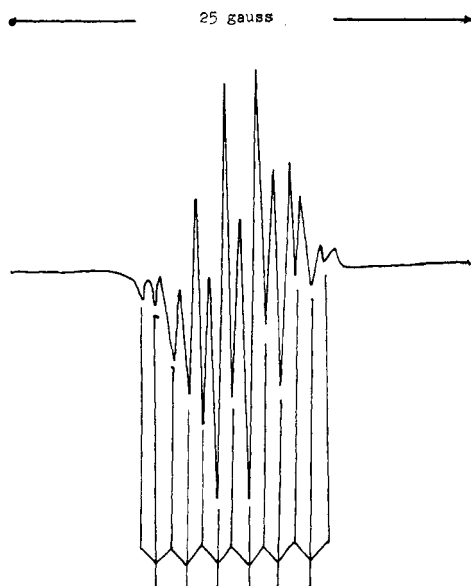
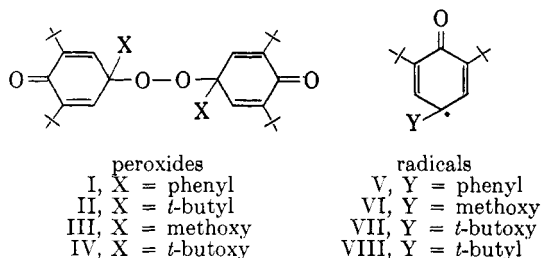


Fig. 1.—First-derivative curve and reconstruction for radical V, A_H phenyl hydrogen = 1.77 gauss, A_H meta hydrogen = 0.88 gauss.

oxide (II) decompose thermally by carbon-oxygen and oxygen-oxygen fission, respectively. We wish to report electron paramagnetic resonance (e.p.r.) studies which confirm these findings and from which we also conclude carbon-oxygen fission to occur on thermal decomposition of bis(1-methoxy-3,5-di-*t*-butyl-2,5-cyclohexadien-4-one) peroxide (III) and bis(1-*t*-butoxy-3,5-di-*t*-butyl-2,5-cyclohexadien-4-one) peroxide (IV).



An approximately 1×10^{-4} M solution of 2,6-di-*t*-butyl-4-phenylphenol⁴ in benzene was oxidized by an aqueous, alkaline potassium ferricyanide solution under 1 atm. of nitrogen to give the magenta-colored benzene solution of the corresponding 2,6-di-*t*-butyl-4-phenylphenoxy radical (V). A sample of the washed and dried (anhydrous Na_2SO_4) benzene layer was sealed in a nitrogen-flushed, 4-mm.-o.d. glass tube and examined in the Varian multipurpose cavity at room temperature. The resulting spectrum and its reconstruction is shown in Fig. 1.

Assuming equal electron spin densities for the five positions of the 4-phenyl group, the 13 lines⁵ may be attributed to the interaction of the odd electron with the *meta* hydrogens and five hydrogens of the 4-phenyl group, *meta*- A_H hydrogens of the cyclohexadien-4-one ring = 0.88 gauss, and 4-phenyl hydrogens = 1.77 gauss. An alternative assignment also consistent with the spectrum and construction of radical V would be *meta*- A_H hydrogens of the cyclohexadien-4-one ring = 1.77 gauss, *ortho*- A_H = *para*- A_H hydrogens of the 4-

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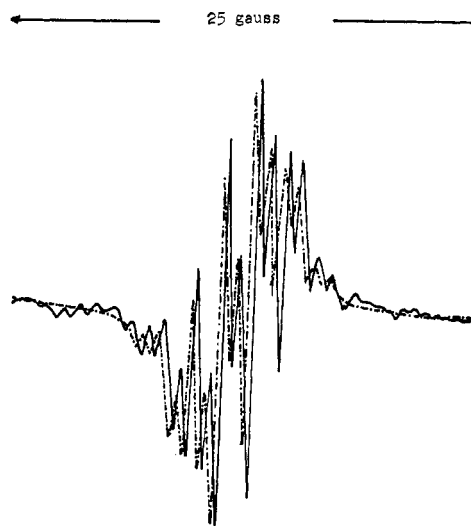


Fig. 2.—First-derivative curve for radical V, —; first-derivative curve for radical from decomposition of peroxide I, - - - - -.

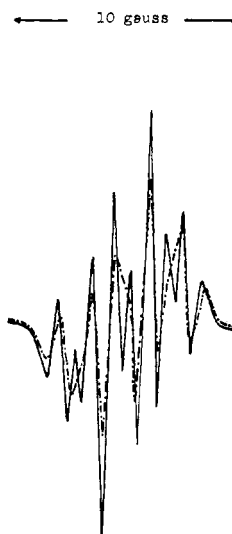


Fig. 3.—First-derivative curve for radical VI, —; first-derivative curve for radical from decomposition of peroxide III, - - - - -.

phenyl ring = 1.77 gauss, and *meta*- A_H hydrogens of the 4-phenyl ring = 0.88 gauss. Thirteen rather than 18 theoretically predicted lines arise from the ratio of the coupling parameters being 2:1. The approximation of 2:1 ratio accounts for the inconsistency between the observed intensity of distribution and the theoretically predicted distribution intensities of 1:2:6:10:15:20:20:20:15:10:6:2:1.

The identity of the spectrum resulting from the thermal decomposition of peroxide I with that of V was established by operation of the dual-sample cavity. The peroxide sample (1×10^{-2} M nitrogen-flushed benzene solution in a 4-mm.-o.d., nitrogen-flushed, sealed tube) was placed in the variable-temperature cavity whose signal was modulated at 400 c.p.s. The other cavity containing the phenoxy radical V was modulated at 100 kc.p.s. The symmetrical 13-line spectrum, shown in Fig. 2, was the sole spectrum observed from the peroxide I between 60–110°.

The identical traces, shown in Fig. 2, implies homolytic carbon-oxygen fission of the symmetrical peroxide I to yield the phenoxy radical V. By a similar proce-

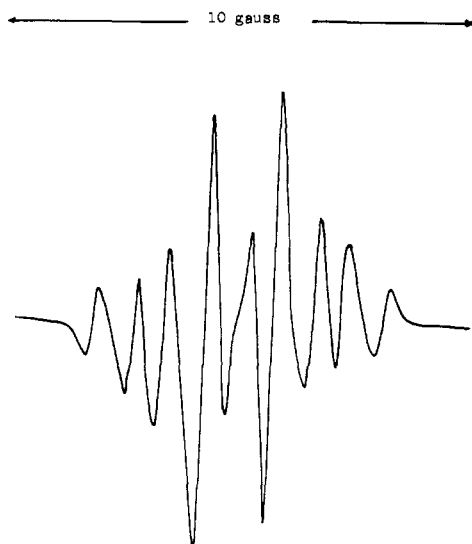


Fig. 4.—First-derivative curve for radical VI at 25°.

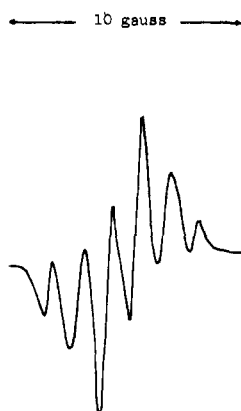


Fig. 5.—First-derivative curve for radical VI at 130°.

ture thermal decomposition of the symmetrical bis-(1-alkoxy-3,5-di-*t*-butyl-2,5-cyclohexadien-4-one) peroxides III and IV were shown to occur by carbon-oxygen fission. As far as we are aware e.p.r. evidence for carbon-oxygen fission in symmetrical bicyclohexadien-4-one peroxides has not been reported, although Turner,⁶ by e.p.r. investigation, had previously shown carbon-oxygen fission to occur on thermal decomposition of an unsymmetrical cyclohexadien-4-one peroxide, namely 2,6-di-*t*-butyl-4-*t*-butylperoxycyclohexa-2,5-dien-1-one.

Oxidation of 2,6-di-*t*-butyl-4-methoxyphenol^{7a} in the presence of oxygen gave the pale yellow, nicely crystalline peroxide III, m.p. 113–114°, lit. 110–111^{7b} and 114–115°. A sample of peroxide III (1×10^{-2} *M* toluene solution) was placed in the variable-temperature cavity of the dual-sample cavity. A measurable signal (modulated at 100 kc.p.s.) was observed when the temperature of the peroxide sample was raised to 130°. In the other cavity, modulated at 400 c.p.s., was placed a sample of the 2,6-di-*t*-butyl-4-methoxyphenoxy radical VI prepared by a similar procedure as for V. The traces resulting from radical VI and decomposition of peroxide III, shown in Fig. 3, are not equivalent in all respects. The spectrum of VI is seen to have nine lines while the

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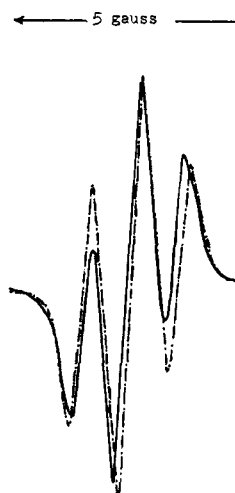


Fig. 6.—First-derivative curve for radical VII, —; first-derivative curve for radical from decomposition of peroxide IV, - - - -.

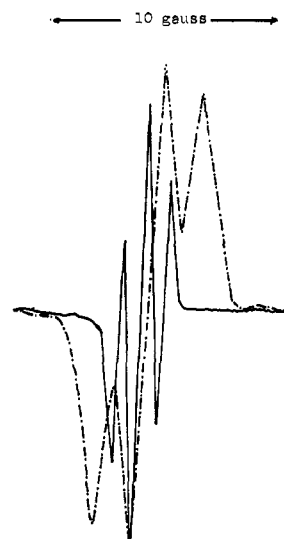


Fig. 7.—First-derivative curve for radical VII, —; first-derivative curve for radical from decomposition of peroxide II, - - - -.

spectrum resulting from decomposition of peroxide III has only six lines. When the sample of 2,6-di-*t*-butyl-4-methoxyphenoxy radical VI was modulated at 100 kc.p.s. at room temperature, the spectrum consisted of nine lines shown in Fig. 4; methyl- $A_H = 1.53$ gauss, *meta*- $A_H = 0.90$ gauss; lit.^{9,10} methyl- $A_H = 1.62$ and 1.6 gauss, *meta*- $A_H = 0.86$ and 1.0 gauss. Since the coupling parameters are approximately in the ratio of 2:1, nine lines with distribution intensities approximately in the ratio of 1:2:4:6:6:6:4:2:1 are obtained. On raising the temperature to 130°, however, the nine-line spectrum gradually degenerates to six lines. The spectrum, shown in Fig. 5, is that recorded for an approximately 1×10^{-4} *M* toluene solution of radical VI at 130° and modulated at 100 kc.p.s. By a comparison of the six-line spectrum, shown in Fig. 3, resulting from the decomposition of peroxide III at 130°, with the six-line spectrum recorded and shown in Fig. 5, for radical VI at the same temperature it is concluded that peroxide III decomposes thermally by homolytic carbon-oxygen fission to give radical VI.

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Oxidation of 2,6-di-*t*-butyl-4-*t*-butoxyphenol in the presence of oxygen gave the cream-colored, nicely crystalline peroxide IV, m.p. 115–116°, lit. 109–109.5°⁷ and 115–116° dec.¹¹ A sample of peroxide IV (1×10^{-2} M benzene solution) was placed in the variable-temperature cavity of the dual-sample cavity and its signal was modulated at 400 c.p.s. In the other cavity, modulated at 100 kc.p.s., was placed a sample of the 2,6-di-*t*-butyl-4-*t*-butoxyphenoxy radical VII prepared by the same procedure as for V. The equivalence of the two spectra, shown in Fig. 6, leads us to conclude that peroxide IV also decomposes thermally by carbon-oxygen fission to give the 2,6-di-*t*-butyl-4-*t*-butoxyphenoxy radical VII; A_H (*meta* ring hydrogens) = 0.99 gauss, lit.¹⁰ A_H (*meta* ring hydrogens) = 1.0 gauss.

In contrast, similar operation of the dual-sample cavity gave no correlation between the spectrum of the 2,4,6-tri-*t*-butylphenoxy radical and the spectrum resulting from thermal decomposition of peroxide II (1×10^{-2} M benzene solution at 100° (see Fig. 7).

The 2,4,6-tri-*t*-butylphenoxy radical VIII was prepared by the same procedure as for V and it gave, when modulated at 100 kc.p.s. in the multipurpose cavity, a 74-line spectrum with A_H (*meta* ring hydrogens) = 1.68 (1.77) gauss, A_H (*para t*-butyl hydrogens) = 0.36 (0.34) gauss, and A_H (*ortho t*-butyl hydrogens) = 0.07 (0.068) gauss. Splitting parameters found by Atherton, *et al.*,¹² are quoted in parenthesis.

A positive radical concentration from the decomposition of a sample of peroxide II prepared from freshly recrystallized II was detected only at temperatures in excess of 60°. Decomposition became rapid at temperatures in excess of 100°. Samples prepared from II which were not recrystallized immediately prior to e.p.r. investigation, however, showed at room temperature an unsymmetrical, unidentified 25-line spectrum.

The symmetrical triplet resulting from the decomposition of peroxide II at 100° (see Fig. 7) was identified to arise from the production of the 2,6-di-*t*-butyl-4-*t*-butoxyphenoxy radical VII in agreement with Pokhodenko and Ganyuk.³ Thus operation of the dual-sample cavity with peroxide II (1×10^{-2} M benzene solution, modulated at 400 c.p.s. at 100°) gave a spectrum which corresponded with the spectrum of radical VII (approximately 1×10^{-4} M benzene solution modulated at 100 kc.p.s.). The traces obtained were almost identical with those produced by carbon-oxygen fission of peroxide IV to give radical VII, shown in Fig. 6. It is thus concluded that peroxide II decomposes thermally by homolytic oxygen-oxygen fission. Additional indirect evidence for oxygen-oxygen fission in peroxide II and carbon-oxygen fission in peroxide IV was obtained by examining previously decomposed samples of peroxides II and IV in the dual-sample cavity. Spectra identical with those shown in Fig. 6 were obtained.

The position of fission in peroxides I, II, III, and IV is suggested to depend chiefly upon how effectively the 1-substituent can stabilize by resonance the radicals that would result from carbon-oxygen fission. In peroxides I, III, and IV the 1-phenyl, 1-methoxy, and 1-*t*-butoxy groups can contribute to the resonance stabilization of

the radicals V, VI, and VII, respectively. However, the 1-*t*-butyl group in peroxide II cannot resonance stabilize radical VIII. Thus, in peroxides I, III, and IV the stability of the product radicals V, VI, and VII would appear to lower the normally higher bond dissociation energy of the carbon-oxygen bond below that of the low dissociation energy of the oxygen-oxygen bond.¹³ In peroxide II, this is not so, since by oxygen-oxygen fission, followed by or concerted with the cleavage and readdition of the 4-*t*-butyl group onto the exocyclic oxygen, the more stable radical VII can be formed.

Electron paramagnetic resonance identification of the radicals observed from the decompositions of peroxides I, II, III, and IV are consistent with carbon-oxygen fission in peroxides I, III, and IV and oxygen-oxygen fission in peroxide II. The position of fission in other symmetrical bicyclohexadien-4-one peroxides is currently being investigated with a view to correlating the position of fission with the resulting radical stability.

Experimental

The preparation of the phenols^{2,4,7a} and peroxides^{5,7} has been previously described. Spin resonance experiments were carried out with a Varian V-4502 e.p.r. spectrometer.

Acknowledgment.—The authors are grateful to the Petroleum Research Fund (Grant No. 1156-44) for financial support of one of the investigators (M. F.) and for a U. S. Public Health Grant (No. GM 10985-02) for the installation of a Varian e.p.r. spectrometer.

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The Preparation of N-Chloroformyl-N-phenylglycine and Its Use in Acylation

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Received May 20, 1964

In the direct phosgenation procedure for the preparation of N-carboxy- α -amino acid anhydrides or 2,5-oxazolidinediones,¹ an intermediate carbamyl chloride or N-chloroformyl derivative forms. In the preparation of 2,5-oxazolidinedione from glycine, Farthing² found that if the solvent were removed at 20° instead of 40°, N-chloroformylglycine resulted. This compound was identified by reaction with aniline to give N-phenylhydantoic acid. The phosgenation of N-*p*-anisylglycine resulted in the isolation of the N-chloroformyl derivative, which failed to cyclize to the anhydride at 40°.³ In the reaction of L-proline with phosgene, N-chloroformyl-L-proline was formed and without isolation was cyclized by reaction with silver oxide in acetone⁴ or

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