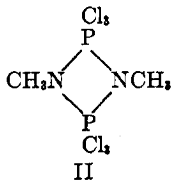
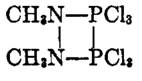
volatile than the dimer, again ruling out higher polymers.

The proton magnetic resonance spectrum of II was obtained in phosphorus oxychloride at 105° to differentiate between the two possible isomeric structures, II and V.[5] The spectrum was a simple


II


V

1:2:1 triplet which would result from the coupling of each proton with two symmetrically disposed phosphorus atoms as in II. The proton magnetic resonance spectrum of V would consist of a doubled doublet—i.e., four lines of equal intensity. This confirms structure II. Chapman *et al.*[3] also proposed structure II on the basis of infrared and Raman spectra and other data.

The unusual stability of this compound, as indicated by its thermal stability and ascribed by Chapman[3] to the delocalization of the ring electrons, is being investigated further.

Michaelis[6] proposed an alternating phosphorus-nitrogen four-membered ring for his phosphinimine dimer ($C_6H_5N—POCl)_2$, and it is likely that the *N*-phenyltrichlorophosphinimine reported by Gilpin[7] was also a dimer containing the same four-membered phosphorus-nitrogen ring.

It seems reasonable that compound II, its homologs, and analogs have previously been formed in other reactions of phosphorus pentachloride and *N*-alkyl- or *N*-arylamides of various organic acids but have gone undetected, either because they occurred only in small amounts, or because the imidoyl chlorides were used without purification.

EXPERIMENTAL

Reaction of N-methyltrifluoroacetamide with phosphorus pentachloride. One hundred and forty grams (1.1 moles) of *N*-methyltrifluoroacetamide and 230 g. (1.1 moles) of phosphorus pentachloride were combined in a 500-ml. round bottomed flask fitted with a Vigreux column and a distillation head leading to a Dry Ice–acetone trap. The reaction vessel was heated to melt the amide and gas evolution commenced immediately. Heating was continued to maintain a brisk evolution of gas. Gas evolution ceased when all the phosphorus pentachloride had dissolved. Heating was continued until the distillate temperature reached 60°.

N-Methyltrifluoroacetimidoyl chloride (I). The condensate in the trap was distilled to give 49 g. of low boiling material and 70 g. (44% yield) of *N*-methyltrifluoroacetimidoyl chloride, b.p. 47–48°/705 mm. The infrared absorption spectrum showed a very strong sharp band at 5.90 μ attributed to the $>C{=}N^-$, and the typical trifluoromethyl group bands in the 8 to 9 μ region.

Anal. Calcd. for $C_3H_3ClF_3N$: C, 24.76; H, 2.07; Cl, 24.37 F, 39.17. Found: C, 24.68; H, 2.28; Cl, 24.62; F, 39.20.

Trifluoroacetyl chloride. The 49 g. of low boiling material, which was recondensed in a Dry Ice–acetone trap, contained an appreciable amount of solid at −78°. An infrared spectrum at 15 mm. pressure of the gas, formed by warming the condensate, was identical with the spectrum of trifluoroacetyl chloride at the same pressure. At 440 mm. pressure the infrared spectrum of the gas from the condensate, gave, in addition to the trifluoroacetyl chloride spectrum, bands at 3.38 μ and 3.54 μ, due to the presence of hydrogen chloride,[8] and a small peak at 5.90 μ, due to the presence of a small amount of *N*-methyltrifluoroacetimidoyl chloride.

Trifluoroacetyl chloride and hydrogen chloride do not form a solid complex at −78°, but *N*-methyltrifluoroacetimidoyl chloride, a liquid at −78°, combines with hydrogen chloride to give a solid which accounts for the solid in the trap at −78°. The solid was warmed slowly from −78° to −20° with no sign of melting or dissociation. Above −20° shrinkage began to occur and at −10° the solid liquified and gas evolution occurred.

1,3-Dimethyl-2,2,2,4,4,4-hexachloro-1,3,2,4-diazadiphosphetidine (II). The residue in the initial reaction vessel was heated on the steam bath under reduced pressure to remove the phosphorus oxychloride, leaving 87 g. (52% yield) of 1,3-dimethyl-2,2,2,4,4,4-hexachloro-1,3,2,4-diazadiphosphetidine, m.p. 170–176°. Sublimation at 140°/0.1 mm., gave II, m.p. 174–179°. When the melt was further heated in the capillary melting point tube gas evolution occurred at 250°.

Anal. Calcd. for CH_3Cl_3NP: C, 7.22; H, 1.82; Cl, 63.93; N, 8.42; P, 18.61. Found: C, 7.63; H, 2.41; Cl, 63.16; N, 8.42; P, 18.46.

Acknowledgment. The authors wish to thank Donald W. Moore and Maynard H. Hunt for their cooperation and helpful discussions on this problem.

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[5] The NMR spectrum of II was recorded and interpreted by Donald W. Moore of this laboratory.

[6] A. Michaelis, *Ann.*, 407, 290 (1915).

[7] J. E. Gilpin, *Am. Chem. J.*, 29, 352 (1897).

[8] R. H. Pierson, A. N. Fletcher, and E. St. Clair Gantz, *Anal. Chem.*, 28, 1239 (1956).

Synthesis of Phenyl-1,2-ethenediol Cyclic Carbonate[1]

L. R. MORRIS AND D. J. HUBBARD

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Previous reports describe the synthesis and polymerization of 1,2-ethenediol cyclic carbonate (I, vinylene carbonate).[2] Compared to other 1,2-disubstituted ethylenes, the ring structure of I appeared to enhance the reactivity in vinyl poly-

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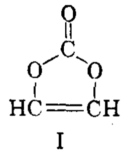
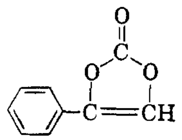
[1] Presented in part before the Division of Organic Chemistry at the 140th National Meeting, American Chemical Society, Chicago, Ill., September 1961.

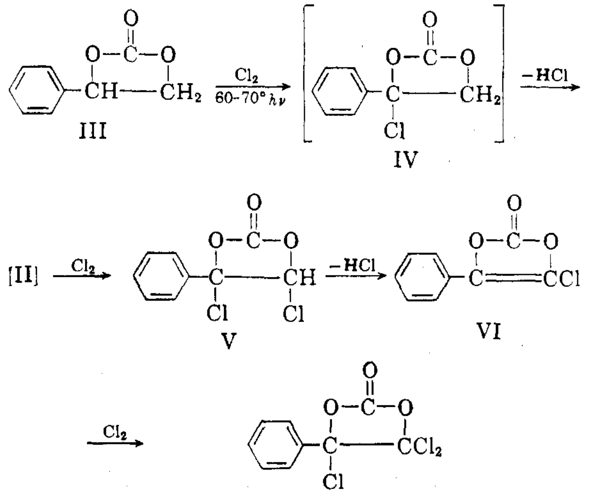
[2] (a) M. S. Newman and R. W. Addor, *J. Am. Chem. Soc.*, 75, 1263 (1953); 77, 3789 (1955). (b) K. Hayashi and G. Smets, *J. Polymer Sci.*, 27, 275 (1958). (c) J. M. Judge and C. C. Price, *J. Polymer Sci.*, 40, 439 (1959). (d) C. G. Overberger, H. Biletch, and R. G. Nickerson, *J. Polymer Sci.*, 27, 381 (1958). (e) W. K. Johnson and T. L. Patton *J. Org. Chem.*, 25, 1042 (1960).

merization. In order to study this cyclic structure more fully, a substituted derivative, phenyl-1,2-ethenediol cyclic carbonate (II) was conceived as a hybrid of both styrene and vinylene carbonate.


I

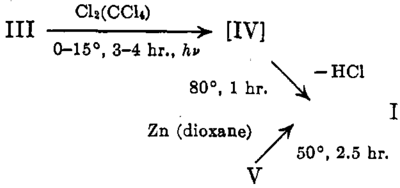

II

By a synthetic approach similar to that described for I,[2a] chlorination of phenyl-1,2-ethanediol cyclic carbonate (III) gave intermediates subsequently converted to the unsaturated carbonate II. Photochlorination of III at 60–70° without a solvent gave a complex mixture, depending upon the extent of chlorination. By using a low distillation temperature during the isolation, a 60% yield of 1,2-dichloro-1-phenyl-1,2-ethanediol cyclic carbonate (V) could be obtained, with small amounts of the corresponding trichloro derivative (VII) as a contaminant. It was found that the fractions of V were usually accompanied by a product only slightly soluble in carbon tetrachloride, proven to be 1-chloro-2-phenyl-1,2-ethenediol cyclic carbonate (VI). Each redistillation of V gave additional amounts of VI, along with hydrogen chloride evolution. Based on previous studies such as the halogenation of dioxane,[3] the following series of reactions was probably involved:



Further confirmation for the above reaction sequence was obtained by chlorination of III at 0–15° in carbon tetrachloride so as to delay the thermal decomposition of the unstable monochloro intermediate IV. Merely heating the resulting chlorination mixture to reflux then caused dehydrochlorination to occur and gave phenyl-1,2-ethenediol cyclic carbonate (II) in about 60% yield.

A second synthesis of II involved zinc dechlorination of V in dioxane. Using either purified or crude samples of V, yields of 20–30% of II were obtained, based on the starting material III.



Phenyl-1,2-ethenediol cyclic carbonate (II) is a fragrant white solid, m.p. 82–83°, essentially insoluble in water, moderately soluble in methanol and carbon tetrachloride, and very soluble in benzene, dioxane, and acetone. Characterization of II included hydrolysis to yield carbon dioxide, elemental analyses, unsaturation analysis, formation of phenylglyoxal 2,4-dinitrophenylhydrazone, and polymerization. Infrared absorptions were consistent with the assigned structure, showing absorptions at 937 and 1805 cm.$^{-1}$, typical of double bond and cyclic carbonate carbonyl groups,[4] respectively. The cyclic carbonate structure of II is stable for some time at the boiling point of 283°, although reaction with air soon turns the liquid brown. This is in contrast to the saturated phenylethanediol carbonate III which decarboxylates at temperatures above 180°, especially when catalyzed by metal oxides or salts such as lithium chloride.[5]

Bromine added readily to the double bond of II to give 1,2-dibromo-1-phenyl-1,2-ethanediol cyclic carbonate as an unstable oil. Attempted distillation of this dibromide was accompanied by decomposition so that essentially all the product was 1-bromo-2-phenyl-1,2-ethenediol cyclic carbonate, m.p. 93–94°, analogous to the chloride VI.

Free radical polymerization of II was found to occur slowly, yielding a polymer with a softening point above 300°. Further details of the polymerization and copolymerization characteristics of this monomer will be the subject of a separate publication.

EXPERIMENTAL[6]

Phenyl-1,2-ethanediol cyclic carbonate (III). This compound was prepared by ester interchange of styrene glycol and diethyl carbonate, similar to the ethylene carbonate synthesis of Morgan and Cretcher.[7] Isolation of III either by distillation or by recrystallization from carbon tetrachloride[8] gave about 85% yields of product, m.p. 53–55°, b.p. 137° (0.8 mm.), and n^{25}_D 1.536.

Chlorination of III *in bulk.* Using Pyrex glassware, a 275-watt General Electric "Sunlamp" was employed as a heat and light source just below the reaction flask. Chlorine was bubbled through concd. sulfuric acid and introduced

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[3] R. K. Summerbell and L. N. Bauer, *J. Am. Chem. Soc.*, **57**, 2364 (1935).

[4] J. L. Hales, J. I. Jones, and W. Kynaston, *J. Chem. Soc.*, 618–625 (1957).

[5] W. J. Peppel, *Ind. and Eng. Chem.*, **59**, 767 (1958).

[6] Melting points are uncorrected.

[7] M. S. Morgan and L. H. Cretcher, *J. Am. Chem. Soc.*, **68**, 783 (1946).

[8] W. K. Johnson, U. S. Patent **2,799,616**, July 1957.

below the surface of the stirred reactants. In a typical experiment, 39.0 g. of III was melted while chlorine addition was maintained for 9 hr. at 60–70° at a rate that gave 7.9 g. increase in weight of the pot contents. Fractionation of the resultant oil was made through a 6-in. Vigreux column. As a forerun, 1.0 g. was collected, b.p. 60–90° (0.3 mm.), $n^{25}\text{D}$ 1.5538, indicated by mass spectroscopy to be *1,2,2-trichloro-1-phenyl-1,2-ethanediol cyclic carbonate* (VII), although further structure proof was not obtained.

Anal. Calcd. for $C_9H_5Cl_3O_3$: Cl, 39.6. Found: Cl, 34.5.

In the second fraction, 11.0 g. was obtained, b.p. 94–107° (0.3 mm.), $n^{25}\text{D}$ 1.5478. After separation of a few crystals, rapid redistillation of the oil gave *1,2-dichloro-1-phenyl-1,2-ethanediol cyclic carbonate* (V) as an unstable oil, b.p. 101–103° (0.2 mm.), $n^{25}\text{D}$ 1.5447.[9] Due to the instability no further purification was achieved.

Anal. Calcd. for $C_9H_6Cl_2O_3$: Cl, 30.5. Found: Cl, 30.2.

A third fraction of the original distillation, 8.4 g., b.p. 110–123° (0.2 mm.), $n^{25}\text{D}$ 1.5464, solidified upon cooling. After two recrystallizations from petroleum ether (b.p. 60–70°), an analytical sample of *1-chloro-2-phenyl-1,2-ethenediol cyclic carbonate* (VI) was obtained, m.p. 99.0–99.5°.

Anal. Calcd. for $C_9H_5ClO_3$: C, 55.0; H, 2.56; Cl, 18.1. Found: C, 55.1; H, 2.60; Cl, 18.0.

A bromate-bromide unsaturation analysis of VI gave only 27% of the theoretical value, typical of highly substituted double bonds. An infrared spectrum of VI showed strong absorption at 1880, 1840, 1220, 1150, 940, and 758 cm.$^{-1}$. Attempted reaction of VI with 2,4-dinitrophenylhydrazine gave only small amounts of a derivative, m.p. 291–293.5°, indicating that phenylglyoxal was not a major hydrolysis product under the acidic conditions. Alkaline hydrolysis, however, readily gave *d,l*-mandelic acid, m.p. 117–119°, upon acidification of the aqueous solution.

Phenyl-1,2-ethenediol cyclic carbonate (II). *Method A.* A solution of 20.0 g. of distilled V in 25 ml. of dioxane was added dropwise to a stirred suspension of 22 g. of zinc (100 mesh) in 75 ml. of dioxane at 50°. After adding about one fourth of the solution in 1 hr., the reaction temperature rose exothermically to 78°. Continued addition at 50° was completed in 1 hr. and was followed by additional stirring for another 30 min. An extraction using ether and about 1 l. of water (slightly acidified with hydrochloric acid) gave a zinc chloride-free ether solution which was concentrated under reduced pressure. The residue was then recrystallized from petroleum ether (b.p. 60–70°) to give 13 g. of product, m.p. 58–75°. After two further recrystallizations, first from petroleum ether and then from carbon tetrachloride, an analytical sample of II was obtained as 5 g. of white crystals, m.p. 82–83°, b.p. 283° or 110° (0.5 mm.).

Anal. Calcd. for $C_9H_6O_3$: C, 66.7; H, 3.73; Cl, 0; mol. wt., 162; unsaturation, 6.17 mmole/g. Found: C, 66.4; H, 3.89; Cl, 0.16; mol. wt., 164 (cryoscopically in benzene); unsaturation, 6.07 mmole/g. (bromate-bromide).

In the infrared spectrum of II strong absorptions were observed as follows: 1805 (side peaks at 1870 and 1830), 1498, 1450, 1139, 1078, 937, and 740 cm.$^{-1}$. After refluxing a sample of II with excess barium hydroxide solution for 6 hr., 106% of the theoretical weight of barium carbonate was isolated by filtration and drying. A reaction of II with 2,4-dinitrophenylhydrazine gave a derivative, m.p. 291–295°, which melted at 292–296° when mixed with known phenylglyoxal 2,4-dinitrophenylhydrazone (m.p. 297–299°). Alkaline aqueous hydrolysis of II gave, after acidification, benzene extraction and solvent removal, a small amount of *d,l*-mandelic acid, m.p. 110–115°. This melted at 115–118° when mixed with known acid of m.p. 118°.

Method B. Similar to Method A, 600 g. of crude, unfractionated product from the chlorination of III was treated with 684 g. of zinc in 1800 ml. of dioxane. After reaction and work-up as described above, 109 g. of II, m.p. 72–77°, was obtained. From the mother liquors about 60 g. of IV was obtained.

Method C. A slurry of 50 g. of III in 300 ml. of carbon tetrachloride was cooled by an ice bath while irradiated from the top with a sunlamp as described for the bulk chlorinations. Addition of chlorine was made over 4 hr., maintaining the pot temperature at 5–10°, until 26 g. of chlorine had been added. After about three fourths of the chlorine was added the system became homogeneous. After addition was complete, nitrogen was flushed through the system for 15 min. and then the solution heated gradually to reflux. Vigorous evolution of hydrogen chloride occurred as the temperature reached 40–50°. With a take-off head attached, about one half of the solvent was removed and the residue cooled to 10° and allowed to stand overnight. Filtration of the solid gave 26 g. (52%) of II, m.p. 78–81°. Analysis of the filtrates indicated another 4 g. of II was present, so a total yield of 60% crude II had been obtained.

1-Bromo-2-phenyl-1,2-ethenediol cyclic carbonate. To a cooled slurry of 8.1 g. of II in 20 ml. of carbon tetrachloride, a solution of 8.0 g. of bromine in 20 ml. of carbon tetrachloride was slowly added with stirring. While keeping the slurry temperature below 10°, the addition was completed in 15 min. and allowed to stand for 5 min. more. All the solid had then dissolved and the solution became clear yellow. Concentration with a rotating evaporator under vacuum at room temperature gave 17 g. of an amber oil, $n^{25}\text{D}$ 1.5778, which had a sharp odor and a tendency to fume when exposed to the air. This sample of *1,2-dibromo-1-phenyl-1,2-ethanediol cyclic carbonate* was used at once and not further purified.

Anal. Calcd. for $C_9H_6Br_2O_3$: Br, 49.7. Found: Br, 47.0.

An aliquot of 12.8 g. of the above dibromide was then distilled *in vacuo* using a 4-in. Vigreux column. Upon heating to 50–70°, vigorous gas evolution occurred, with some reddish vapors of bromine (0.5 g.) being collected in the Dry Ice trap. All the distillate was collected in one fraction, b.p. 108–114° (0.5–1 mm.), 7.9 g. (88%) of white solid. Two recrystallizations from petroleum ether (b.p. 60–70°) gave 4.3 g., m.p. 93–94°.

Anal. Calcd. for $C_9H_5BrO_3$: Br, 33.2. Found: Br, 33.2.

A close similarity of the infrared spectrum of this bromide with that of VI was found, with strong absorptions at 1870, 1830, 1200, 1130, and 938 cm.$^{-1}$.

Decarboxylation of cyclic carbonates. When a sample of III mixed with 5% powdered lithium chloride was heated, gas evolution started at 180° and was quite rapid at 200°. Under the same conditions, a mixture of II and lithium chloride gave no gas liberation, even at 250°. As observed in most reactions of II in the presence of air, a brown color developed during the heating.

Polymerization of II. Upon being heated with peroxidic or azo-type free radical catalysts, either in bulk or in solution, II slowly polymerized to give a product soluble in dioxane and precipitated by ethanol. This polymer, softening above 300°, showed infrared absorptions at 1833, 1450, 1332, 1178, 750, and 696 cm.$^{-1}$. A reddish brown polymer insoluble in ethanol was produced when II was treated with aluminum chloride. Further details of the polymerization characteristics of II will be the subject of a separate publication.

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(9) A similar relationship of decreasing boiling points with increasing chlorine substitution was observed by Newman and Addor[2a] in the chlorinated ethylene carbonates. This may be due to diminished molecular association as the heterocyclic hydrogens are progressively removed.