

Preparation of 3-Amino-2-fluoropropene.—I, 45.0 g, and 107 g of ammonia were heated in a stainless steel bomb at 60° for 15 min. Distillation gave 14.0 g of 3-amino-2-fluoropropene, bp 70°, n_D^{20} 1.4029. The structure was confirmed by ir spectrum [bands at 2.97, 3.05, and 6.20 (NH₂), 3.24 and 3.32 (=CH₂), 5.97 (=CF-)], and by mass spectrum, mol wt 75. The neutral equivalent was 76.9, with the theoretical 75.08.

Copolymerization of I.—Equimolar amounts of I and acrylonitrile were reacted at 25° using diisopropylperoxy dicarbonate as a catalyst. A 50% yield of pale yellow powder was produced which contained 32% of I and had a reduced viscosity of 0.40.

A copolymer with methyl methacrylate prepared in the same way had a reduced viscosity of 0.048, and contained 46% by weight of I.

Registry No.—I, 6186-91-0; II, 420-97-3; III, 420-44-0; 2-fluoropropene, 1184-60-7; 2-fluoro-3-iodopropene, 5675-33-2; 2-fluoro-2-propenyl ethyl ether, 407-51-2; 2-fluoro-2-propenol, 5675-31-0; 3,5-dinitrobenzoate ester of 2-fluoro-2-propenol, 26332-84-3; 3-amino-2-fluoropropene, 5675-32-1.

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Mass Spectra and Pyrolyses of *o*-Phenylene Carbonate and Related Compounds^{1a,b}

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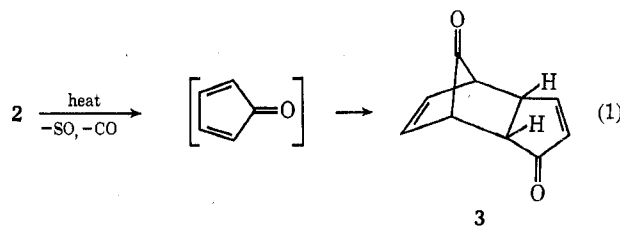
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The mass spectra of *o*-phenylene carbonate (1) and its 4-methyl (4), 4-chloro (5), and 4,5-dichloro (6) derivatives show the loss of CO₂ followed by CO to be the major fragmentation of the molecular ion, supported by metastable peaks. A minor path, without metastable peaks, involves successive losses of CO for a total of 3CO lost. When 1 is pyrolyzed by sweeping it in a stream of nitrogen through a 12-in. hollow quartz tube heated by an electric furnace, indene (13%) and naphthalene (16%) are the major products at 875°. If methanol is introduced into the stream, an intermediate ketene resulting from loss of CO₂ from 1 is trapped and is isolated as dimers of methyl cyclopentadiene-1-carboxylate (7, 44% at 810°); a dimer (3) of cyclopentadienone which forms by loss of 2CO from 1 is also isolated, but in lower yield (14% at 810°). The pyrolytic results from 1 are compared with its mass spectrum and with the results of the pyrolysis of *o*-phenylene sulfite (2). Thus compound 1 exhibits similarities between its pyrolytic and electron-impact reactions, indicating that there are electronic relationships between the two processes. The 4-methyl and 4-chloro derivatives of 1 were also pyrolyzed, without attempts being made to trap intermediates.

The mass spectra of a number of organic carbonates have been compared with the products isolated from their pyrolyses, and similarities and differences have been noted. For example, the mass spectrum of ethyl phenyl carbonate shows the loss of CO₂ from the molecular ion, followed by the loss of C₂H₄ to give the base peak at m/e 94 which is likely the molecular ion of phenol;² in comparison, the pyrolyses of ethyl aryl carbonates yield C₂H₄, CO₂, and the corresponding phenol.³ The molecular ions of diaryl carbonates also eliminate CO₂, presumably giving molecular ions of diaryl ethers.² The pyrolysis of diphenyl carbonate gives CO₂, phenol, diphenyl ether, and other products; however, diphenyl carbonate appears to rearrange to 2-phenoxybenzoic acid from which the pyrolytic products are formed.⁴

In the mass spectrum of *o*-phenylene carbonate (1), the molecular ion fragments losing CO₂, followed by CO.⁵ The electron-impact and pyrolytic reactions of a related compound, *o*-phenylene sulfite (2), have been

reported.⁶ The mass spectrum of 2 shows the successive losses of SO and 2CO from the molecular ion; the most intense fragment peak corresponds to elimination of SO followed by CO. Upon pyrolysis of 2, the Diels-Alder dimer (3) of cyclopentadienone is obtained in 30% yield (eq 1). Thus, both the pyrolytic and electron-impact reactions of 2 proceed *via* losses of SO and CO. The pyrolysis of 1 has not been reported.



We have determined the pyrolytic and electron-impact reactions of *o*-phenylene carbonate (1) in order to determine if similarities exist. A comparison with *o*-phenylene sulfite (2) was also made. We report our results in this article.

Results

Mass Spectra of *o*-Phenylene Carbonates.—*o*-Phenylene carbonate (1) and its 4-methyl (4), 4-chloro (5), and 4,5-dichloro (6) analogs have been prepared and their mass spectra have been obtained. The 70-eV mass spectrum of 1 is shown in Figure 1. The major fragmentation path in the mass spectra of 1 and 4-6 is the

(6) D. C. DeJongh, R. Y. Van Fossen, and C. F. Bourgeois, *Tetrahedron Lett.*, 271 (1967).



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(1) (a) This investigation was supported in part by the Alfred P. Sloan Foundation, 1967-1969. (b) This manuscript was taken in part from the Ph. D. Dissertation of D. A. Brent, Wayne State University, Detroit, Mich., 1970. (c) D. A. Brent acknowledges the financial support of the Frank Knoller and Detroit News Research Fellowships.

(2) P. Brown and C. Djerassi, *J. Amer. Chem. Soc.*, **88**, 2469 (1966).

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TABLE I
PER CENT RELATIVE INTENSITY OF THE (M⁺ - XO₂) AND (M⁺ - XO)
PATHS FOR o-PHENYLENE CARBONATE (1) AND o-PHENYLENE SULFITE (2)

(X = S or C; 70-eV mass spectra)

Compd	M ⁺	M ⁺ - XO ₂	M ⁺ - XO ₂ - XO	M ⁺ - XO	M ⁺ - 2XO	M ⁺ - 3XO
1	80.0	58.5	100	0.3	1.8	14.3
4 (4-CH ₃)	70.0	58.3	100		1.9	10.8
5 (4-Cl)	91.0	58.0	100	0.5	3.5	0.5
6 (4,5-di-Cl)	100	44.0	59.0		2.3	2.5
2 ^a	100	6.5	20.7	40.0	98.0	64.2

^a See ref 6.

loss of CO₂ from the molecular ion followed by the loss of CO; this path is supported by the presence of appropriate metastable peaks. These spectra also exhibit a minor competing path, namely, the successive loss of three molecules of CO, although there are no metastable peaks for these transitions. The relative intensities of these (M⁺ - CO₂) and (M⁺ - CO) paths are given in Table I and compared with the corresponding data on the (M⁺ - SO₂) and (M⁺ - SO) paths in the mass spectrum⁶ of o-phenylene sulfite.

Thus, in the mass spectra of these o-phenylene carbonates, the loss of CO₂ from the molecular ions is favored over the loss of CO, whereas the loss of SO is favored over the loss of SO₂ from the molecular ions of o-phenylene sulfite (2). The major paths are accompanied by relatively intense metastable peaks, whereas no metastable peaks are present for the minor paths. Low voltage (14–20 eV) data were obtained from 1 and 4–6 to determine if there is an enhancement of the (M⁺ - CO) path relative to the (M⁺ - CO₂) path as the energy of the bombarding electrons is lowered; no enhancement is observed.

Mass-spectrometric electrocyclic reactions exhibiting normal metastable peaks are postulated to be analogous to pyrolytic processes.^{7,8} On this basis, one would predict that carbonate 1 should initially lose CO₂ upon pyrolysis and that sulfite 2 should initially lose SO, if the pathways are electrocyclic. The latter prediction has been confirmed (eq 1)⁶ and the first prediction is discussed in the following section.

Pyrolysis of o-Phenylene Carbonate.—o-Phenylene carbonate (1) was pyrolyzed by sweeping it in a stream of nitrogen through a 12-in. hollow quartz tube heated by an electric furnace. The pyrolysis was carried out over a wide range of temperatures, and the products were separated and isolated by glpc. Pyrolysis begins to occur at approximately 600°, and no starting material is recovered above 800°. In the range of 700–760°, the products are starting material, an orange polymer, and small quantities of indene, naphthalene, and cyclopentadienone dimer (3). In the 760–875° range, indene and naphthalene are the major products. The use of helium as carrier gas in place of nitrogen does not affect the results substantially. At 780° indene and naphthalene were obtained in 10.4 and 9.5% yield, respectively, and at 875°, in 13.0 and 15.7% yield.⁹ Minor amounts of styrene, phenylacetylene, azulene, dimer 3, and phenanthrene were identified also.

(7) R. C. Dougherty, *J. Amer. Chem. Soc.*, **90**, 5780 (1968).(8) D. A. Brent, J. D. Hribar, and D. C. DeJongh, *J. Org. Chem.*, **35**, 135 (1970).

(9) In computing these yields, it was assumed that 2 mol of 1 are required to produce 1 mol of product.

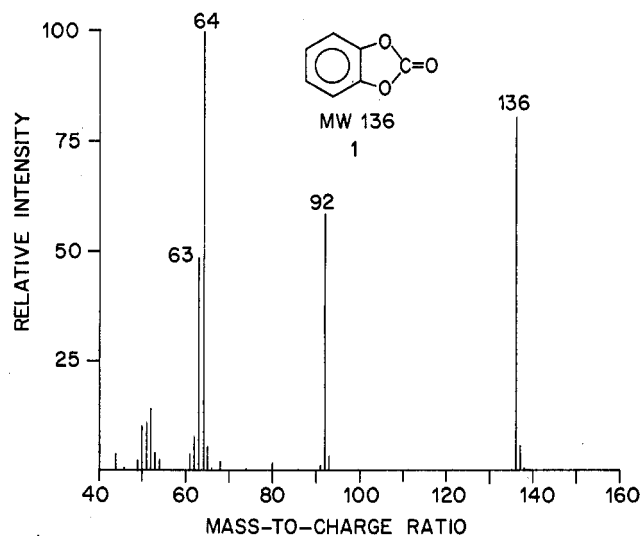
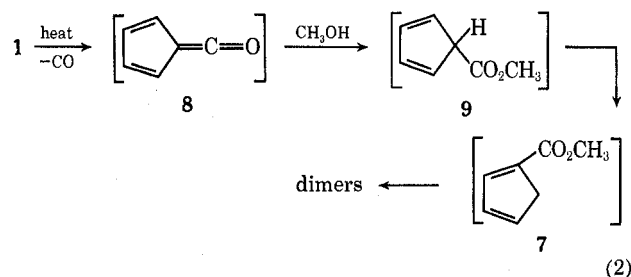


Figure 1.—Mass spectrum (70 eV) of o-phenylene carbonate (1).

If methanol is introduced into the flow before it enters the furnace, aromatic hydrocarbons, polymer of formaldehyde, dimer 3, and a trapped intermediate are isolated. The insoluble orange material is not formed. By selecting the proper pyrolytic conditions, the amount of trapped adduct can be maximized.

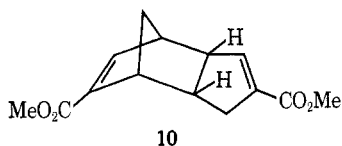
The trapped product has been identified as dimers of methyl cyclopentadiene-1-carboxylate (7), formed from interception of the intermediate 8 with methanol (eq 2).



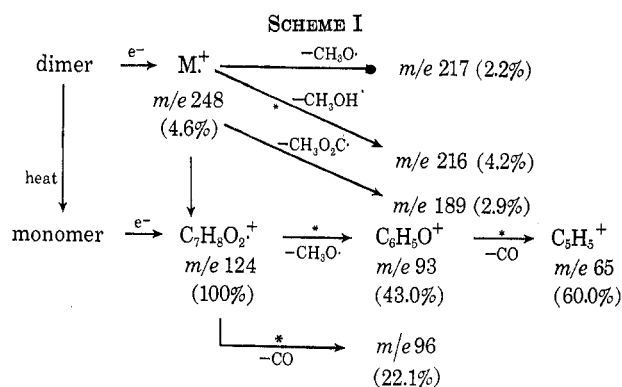
Other attempts to synthesize carboxylate 9 have also resulted in its rearrangement to the more stable conjugated isomer 7, which dimerizes.^{10–13} The ir spectrum of the trapped intermediate exhibits carbonyl absorption at 1725 cm⁻¹. The overall features of its nmr spec-

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trum are consistent with those reported¹² for dimer 10, the major component of the mixture of isomeric dimers of 7.



In the mass spectrum of the trapped material, the base peak, m/e 124, is due to a retro-Diels-Alder reaction induced by electron impact and/or by heat in the inlet system or ion source; at higher temperatures, a mass spectrum of the monomer only is obtained. The fragmentation is summarized in Scheme I. The ele-



mental compositions of the ions at m/e 124, 93, and 65 (Scheme I) agree with the theoretical values within ± 1.0 mmu. The source temperature used for peak matching was 180°, too high to allow for detection of dimer ions. The data in Scheme I were obtained *via* a direct probe at 100° and 70 eV.

When 2.00 g of 1 was pyrolyzed at 840° under trapping conditions with methanol, 0.48 g of recovered 1, 34% of dimers of 7, and 10% of dimer 3 were isolated, along with minor amounts of various aromatics. At 800–820°, the values were 0.66 g of 1 recovered, 44% of dimers of 7, and 14% of dimer 3.

Pyrolyses of 4-Methyl (4) and 4-Chloro (5) Derivatives of 1.—When 4-methyl-*o*-phenylene carbonate (4) is pyrolyzed at 820° under the conditions described for the pyrolysis of 1, the major products isolated by glpc are toluene (10%), indene (4%), naphthalene (3%), styrene (3%), and phenylacetylene (1%). These products were identified by comparison of their retention times and mass spectra with those of authentic samples. An insoluble orange-brown material was also formed. Minor products collected by glpc have mass spectra consistent with trimethylbenzene, xylene, methylstyrene, methylindene, methylnaphthalene, dimethylnaphthalene, and biphenyl, but these minor products were not identified unequivocally. No trapping experiments were attempted.

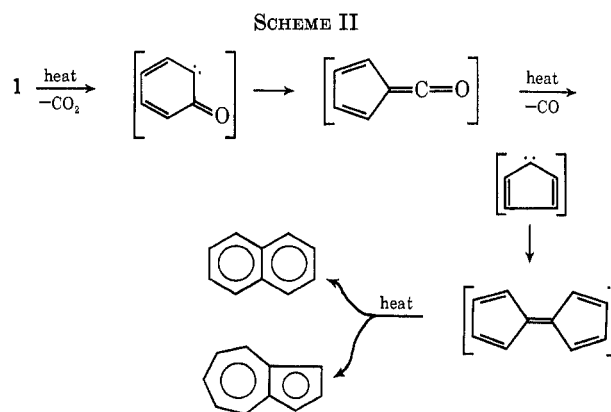
Pyrolysis of 5 at 780–820° leads to a number of products in addition to an insoluble orange-brown solid. Mass spectra were taken of materials collected by glpc. The chlorine isotopic clusters and the m/e ratios suggest the following assignments for the products: phenylacetylene; monochloro- and dichlorophenylacetylene; monochloro-, dichloro-, and trichloronaphthalene; and monochlorobiphenylene. These products were not

identified further and yields were not calculated. No trapping experiments were attempted.

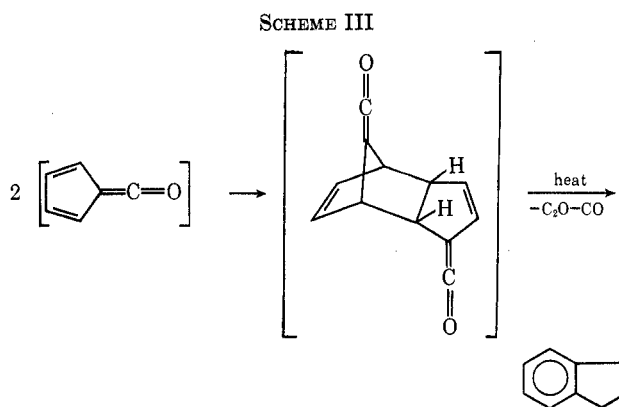
The 4,5-dichloro derivative (6) was not pyrolyzed.

Discussion

The major products from the gas phase pyrolysis of *o*-phenylene carbonate are indene and naphthalene, with minor amounts of aromatics among which is azulene. Naphthalene and azulene could form, at least in part, from a pyrolytic gas phase rearrangement of fulvalene, as shown in Scheme II. In another study,



naphthalene, azulene, and an unidentified red oil were isolated after an attempt to synthesize fulvalene by the dehydrogenation of bicyclopentanes at 300–400° over 5% Pd-C,¹⁴ suggesting that the three C₁₀H₈ isomers are related thermally. This pathway is similar to the (M⁺ - CO₂ - CO) path in the mass spectrum of 1. Likewise, one could propose that indene forms *via* dimerization of the ketene followed by loss of C₂O¹⁵ and CO (Scheme III).



However, the aromatic compounds isolated from the pyrolysis of 1 are also isolated from other high-temperature pyrolyses.^{16–18} Their formation has been attributed to prior degradation of the starting materials to simple molecules such as acetylene and butadiene followed by recombination.^{17,18} Thus, in the pyrolysis of 1, it is not possible to say how much of the yields of

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(15) H. B. Palmer and T. J. Hirt, *J. Amer. Chem. Soc.*, **84**, 113 (1962).

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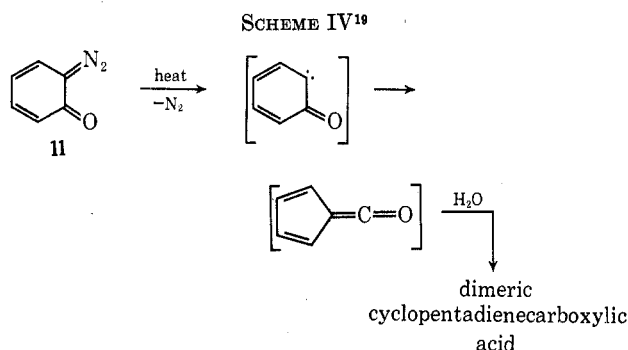
(17) A. Hagemann, *Angew. Chem.*, **42**, 355 (1929).

(18) G. M. Badger, *Progr. Phys. Org. Chem.*, **3**, 1 (1966).

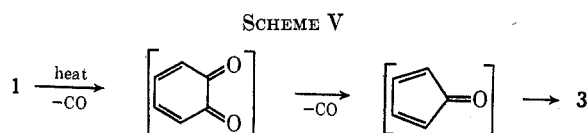
naphthalene and azulene form *via* the fulvalene route, if any, and how much form *via* pyrolytic degradation and recombination.

Support for the possibility that indene and naphthalene are formed, at least in part, *via* degradation-recombination can be found in the products obtained from the pyrolyses of the 4-methyl (4) and 4-chloro (5) derivatives of 1. For example, mono-, di-, and trichloronaphthalene are formed from 5, rather than just the dichloronaphthalene predicted by the route in Scheme II. Likewise, indene and naphthalene are formed in the pyrolysis of 4 as well as from 1.

In order to demonstrate that the route proposed in Scheme II is at least partially correct, we trapped the intermediate ketene with methanol in high yield. The liquid phase pyrolyses of aromatic *o*-diazo oxides have been reported,^{19,20} and the proposed intermediates are the same as those we have proposed for the loss of CO₂ from 1 (Scheme IV). The products trapped in the pyrolyses of 1 and 11 indicate that they do indeed form a common intermediate ketene.



Dimer 3 is also produced in the pyrolysis of 1, presumably *via* the route in Scheme V, competing with the CO₂ path in Scheme II. A rough estimation of the im-



portance of the (M⁺ - CO₂) path *vs.* the (M⁺ - CO) path in the mass spectrum of 1 can be obtained by summing the relative intensities of each of these paths (Table I). The (M⁺ - CO₂) path is favored by a factor of 10. The relative yields of dimers of 7 to dimer 3, in the pyrolysis of 1 in the presence of methanol, show the CO₂ path in Scheme II to be favored over the CO path in Scheme V by a factor of 3, although only a crude ratio of the importance of the two competing paths under pyrolytic conditions can be expected to be obtained.

A comparison of the electron-impact and pyrolytic reactions of *o*-phenylene carbonate and *o*-phenylene sulfite⁶ is of interest. An empirical method which has been used with some success in predicting mass-spectral fragmentations is to choose the path which gives the most stable positively charged and neutral fragments. The losses of CO₂ from the molecular ion of *o*-phenylene car-

bonate (1) and of SO₂ from the molecular ion of *o*-phenylene sulfite (2) give C₆H₄O⁺, and there is no obvious reason why the ions should not be identical from both molecules. The same logic can be applied to the losses of CO from 1 and of SO from 2, giving C₆H₄O₂⁺. Thus, differences cannot be explained easily on the basis of ion stability. Perhaps they might be due to the relative stabilities of the neutral species eliminated. The heats of formation of CO, CO₂, SO, and SO₂ provide a relative estimation of their stability. The reported values²¹ of their heats of formation follow: CO, -25,400; CO₂, -93,690; SO, +19,250; and SO₂, -70,980 g cal/mol. One would predict on this basis that, if CO₂ is lost from the carbonate, SO₂ should be lost from the sulfite. However, the predominate mass-spectrometric path for the sulfite is loss of SO and for the carbonate, CO₂. Likewise, one would predict the predominant initial pyrolytic fragmentation of the carbonate to be CO₂ and the sulfite to be SO₂. However, the predominant pyrolytic path for the sulfite involves the initial loss of SO and for the carbonate, CO₂.

Perhaps differences between the behavior of the sulfites and carbonates upon electron impact and pyrolysis are related to the propensity of sulfur compounds to rearrange. The sulfite might rearrange to an intermediate, the analog of which is inaccessible to the carbonate, in which the elimination of SO is favored over SO₂. For example, benzothiophene 5,5-dioxide eliminates SO pyrolytically as well as from its molecular ion;²² this elimination has been explained by a rearrangement of -SO₂- to -O-SO-.

Compound 1 exhibits similarities between its pyrolytic and electron-impact reactions, indicating that there are electronic relationships between the two processes. Compound 2 does also. As of now, these relationships remain undefined.

Experimental Section

Infrared spectra were recorded with a Perkin-Elmer Infracord. Nmr spectra were determined on a Varian A-60 spectrometer, using CDCl₃ or CCl₄ as solvents and TMS as an internal standard. Mass spectra were obtained from an Atlas CH₄ or an AEI MS902 mass spectrometer. The high resolution data were obtained with the AEI MS902 mass spectrometer set at 10,000 static resolution (10% valley); theoretical and experimental values agree within ± 1.0 mmu. All glpc work was, unless otherwise indicated, carried out with a Hewlett-Packard 5750 research chromatograph with a thermal conductivity detector. Ultraviolet and visible spectra were determined with a Perkin-Elmer 202 or Cary 14 spectrophotometer. Chemical analyses were carried out by Midwest Microlab, Inc., Indianapolis, Ind.

Preparation of *o*-Phenylene Carbonate (1).—*o*-Phenylene carbonate (1) was prepared by a method modified from that reported.²³ Approximately 6.8 g of sodium hydroxide was added to 19 ml of deaerated water. The solution, under nitrogen, was cooled to 5°. Then 8.5 g of catechol (Aldrich) was dissolved in the sodium hydroxide solution. Toluene, 50 ml, was added forming a heterogeneous system. The mixture was cooled to 0–5°. Phosgene (J. T. Baker) was slowly bubbled through the mixture for 1 hr. The mixture was stirred under nitrogen at 5° for another hour, after which the reaction was allowed to come to ambient temperature. The solution was filtered and the toluene layer was evaporated to dryness. (Unreacted phosgene may still be present in the toluene at this point. Therefore, evaporation was carried out in the hood.)

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(20) J. de Jonge, R. J. H. Alink, and R. Dijkstra, *Recl. Trav. Chim. Pays-Bas*, **69**, 1448 (1950).

(21) "Handbook of Chemistry and Physics," 49th ed, The Chemical Rubber Co., Cleveland, Ohio, 1968, p D-22.

(22) E. K. Fields and S. Meyerson, *J. Amer. Chem. Soc.*, **88**, 2836 (1966).

(23) R. S. Hanslick, W. F. Bruce, and A. Mascitti, "Organic Syntheses," Coll. Vol. IV, Wiley, New York, N. Y., 1963, p 788.

The residue was washed several times with small portions of cold methanol to remove traces of catechol. The product was dried overnight in a vacuum desiccator over Drierite at 10 mm, then sublimated at 80° (1 mm). A 75% yield of *o*-phenylene carbonate was obtained, mp 119–120° (lit.²³ 119–120°). A singlet at δ 7.25 was observed in the nmr. The ir spectrum contains intense absorptions at 1835 and 1240 cm⁻¹. The mass spectrum is presented in bar graph form in Figure 1.

Anal. Calcd for C₇H₄O₃: C, 61.76; H, 2.97. Found: C, 61.52; H, 3.22.

Preparation of 4-Methyl-*o*-phenylene Carbonate (4).—The procedure described for *o*-phenylene carbonate was used in the reaction of 4-methylcatechol (Aldrich) with phosgene. After the majority of toluene was evaporated, the resulting solution was vacuum distilled at 0.5 mm. Two fractions (65–75° and 85–95°) show hydroxyl as well as carbonate absorption bands in their ir spectra. The fraction boiling at 65–75° was further purified *via* preparatory glpc. A Hewlett-Packard 776 preparative gas chromatograph with a flame detector and 8 ft × 1 in. 15% Carbowax 20M column was used; injection port 290°, oven 160°. 4-Methyl-*o*-phenylene carbonate (4) was obtained, mp 32–33°. The ir spectrum contains intense absorptions at 1850 and 1245 cm⁻¹. Its mass spectrum is summarized in Table I.

Preparation of 4-Chloro-*o*-phenylene Carbonate (5).—The procedure described for *o*-phenylene carbonate was used in the reaction of 4-chlorocatechol (Chemical Procurement Laboratories) with phosgene. The liquid remaining after removal of toluene was separated by glpc using a 12 ft × 1/4 in., 10% Carbowax 20M column programmed 75–210°. The major components of the liquid, in addition to residual toluene, were collected and analyzed by mass spectrometry. The components are *o*-phenylene carbonate and 4-chloro-*o*-phenylene carbonate (*m/e* 170, 126, 98, and 63). Apparently the 4-chlorocatechol contained catechol as an impurity. Pure samples of 4-chloro-*o*-phenylene carbonate were collected *via* glpc, mp 66–68°, yield 52%. The ir spectrum of 4-chloro-*o*-phenylene carbonate contains intense absorptions at 1860 and 1240 cm⁻¹. The mass spectrum is summarized in Table I.

Anal. Calcd for C₇H₃ClO₃: C, 49.28; H, 1.78; Cl, 20.80. Found: C, 49.21; H, 1.80; Cl, 20.53.

Preparation of 4,5-Dichloro-*o*-phenylene Carbonate (6).—A procedure modified from the one described for *o*-phenylene carbonate was used to react 4,5-dichlorocatechol (K & K Laboratories, recrystallized from carbon disulfide prior to use) with phosgene. To a solution of 2 g of sodium hydroxide in 10 ml of deaerated water (under nitrogen), 2.28 g of 4,5-dichlorocatechol was dissolved. Approximately 100 ml of toluene was added, and the mixture was cooled to 0–5°. Phosgene was slowly bubbled through the solution for 45 min. The toluene at this point was yellow and a white precipitate was evident. The solution was stirred at 0–5° for 25 min and then allowed to come to room temperature. The reaction mixture was worked up as described previously. The product was purified by sublimation at 80° (1 mm). A yield of 2.2 g (84%) of 4,5-dichloro-*o*-phenylene carbonate was obtained, mp 98–99° (lit.²⁴ 76–77°). The ir spectrum contains intense absorptions at 1855 and 1245 cm⁻¹. The mass spectrum of 4,5-dichloro-*o*-phenylene carbonate is summarized in Table I.

Anal. Calcd for C₇H₂Cl₂O₃: C, 41.00; H, 0.99; Cl, 34.60. Found: C, 41.02; H, 1.14; Cl, 34.35.

Although the melting point for this compound is higher than the one reported in the literature,²⁴ the other physical data are consistent with its structure.

Pyrolysis Apparatus and Procedure.—The pyrolysis apparatus and procedure have been described elsewhere.⁸ In the trapping experiment, methanol was added at the point the stream enters the heated area. Methanol introduced at the exit was ineffective in trapping the intermediate.

Pyrolysis of *o*-Phenylene Carbonate (1).—Table II summarizes the conditions and results of six pyrolyses of 1. Glpc using a Carbowax 20M liquid phase is the best method for separating products. The products were quantitatively analyzed by comparison of the area under the glpc curves (by weighing) with those produced by a standard solution of the compound. The assumption was made that 2 mol of 1 are required to produce 1 mol of naphthalene or indene. Nine other pyrolyses were carried out under a variety of conditions, also.

TABLE II
CONDITIONS AND RESULTS OF THE PYROLYSES
OF *o*-PHENYLENE CARBONATE (1)

1, g	Gas flow or system pressure, carrier gas	Temp, °C	% indene	% naphthalene
1.5	10 mm, N ₂	760–810 ^a	7.1	9.3
2.1	5 mm, He	760–785	7.8	11.5
2.0 ^b	0.6 l./min, N ₂	740	0.9	0.2
2.0	0.7 l./min, N ₂	780	10.4	9.5
2.0	0.4 l./min (12 mm), N ₂	800	7.6	5.6
2.0	0.7 l./min, N ₂	875	13.0	15.7

^a The tube was packed with Vycor tubing in the heated area in this pyrolysis only. ^b In this pyrolysis, 1.17 g of starting material was recovered.

Indene was identified by the correlation of its retention time and ir and mass spectra with those of an authentic sample. Naphthalene was identified similarly and by its melting point. Minor amounts of styrene, phenylacetylene, azulene, dimer 3, and phenanthrene are formed also. These were identified by comparison of their retention times, and their ir spectra (or visible spectrum in the case of azulene) and mass spectra with those of authentic samples.

Trapping of a Pyrolytic Intermediate from 1 with Methanol.—Two typical trapping experiments are summarized in Table III. The nmr, ir, and mass spectra of the dimers of 7 were obtained and pertinent items are discussed in the results section. Dimer 3 was identified by comparison of its retention time, and ir and mass spectra with those of an authentic sample.^{5,6}

TABLE III
PYROLYSIS OF *o*-PHENYLENE CARBONATE (1)
IN THE PRESENCE OF METHANOL

1, g	N ₂ flow, pressure	Temp, °C	% of 3	% dimers of 7	Recovered 1, g
2.0	0.8 l./min, 16 mm	800–820	14	44	0.66
2.0	0.8 l./min, 15 mm	840	10	34	0.48

Pyrolysis of 4-Methyl-*o*-phenylene Carbonate (4).—4-Methyl-*o*-phenylene carbonate was pyrolyzed at 820° with a flow rate of 0.8 l./min and a system pressure of 2.8 mm. A chloroform solution of the products was worked up by glpc using a 12 ft × 0.25 in. 10% Carbowax 20M column. An orange-brown insoluble solid remained in the air trap. The major products are toluene (10%), styrene (3%), indene (4.3%), phenylacetylene (1.2%), and naphthalene (2.5%); their retention times and mass spectra correspond to those of authentic samples. Mass spectra of minor products result in the following tentative assignments: xylene (*m/e* 106), trimethylbenzene (*m/e* 120), methylstyrene (*m/e* 118), methylindene (*m/e* 130), methyl-naphthalene (*m/e* 156), dimethyl-naphthalene (*m/e* 156), and biphenyl (*m/e* 154).

Pyrolysis of 4-Chloro-*o*-phenylene Carbonate (5).—Approximately 1.5 g of 4-chloro-*o*-phenylene carbonate was pyrolyzed at 780–820°. The nitrogen flow was 0.9 l./min (6–10 mm). The chloroform solutions of the pyrolysis products were worked up by glpc using a 3 ft × 0.25 in. 5% Carbowax 20M column programmed 80–210°. An orange-brown chloroform-insoluble solid remained in the air and liquid nitrogen traps.

Mass spectra were taken on the materials collected *via* glpc. The mass spectra are simple; *i.e.*, they contain mainly molecular ions, which is typical of aromatic compounds. The chlorine isotopic clusters and the *m/e* ratios suggest the following tentative assignments: phenylacetylene (*m/e* 102), monochloro-phenylacetylene (*m/e* 136), dichlorophenylacetylene (*m/e* 170), monochloronaphthalene (*m/e* 162), dichloronaphthalene (*m/e* 196), trichloronaphthalene (*m/e* 230), and monochlorobiphenylene (*m/e* 186).

Registry No.—1, 2171-74-6; 4, 26358-44-1; 5, 26308-79-2; 6, 704-75-6.

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