Acknowledgment.—We wish to thank the following members of the Physical Chemistry Department under the direction of Dr. P. Bommer: Dr. F. Scheidl for the microanalyses, Dr. T. Williams for the nmr spectra, Dr. V. Toome for the uv spectra, and Mr. S. Traiman for the ir spectra.

Mass Spectra and Pyrolyses of Tetrachloro-*o*-phenylene Carbonate and Tetrachloro-*o*-benzoquinone[1a,b]

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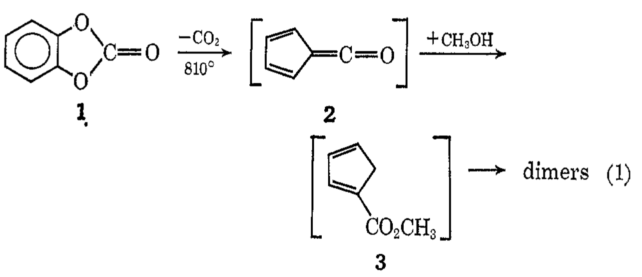
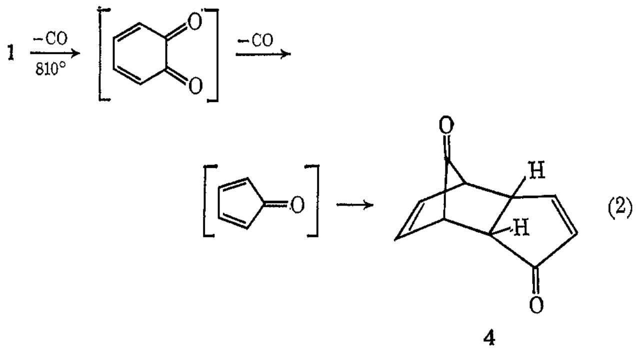
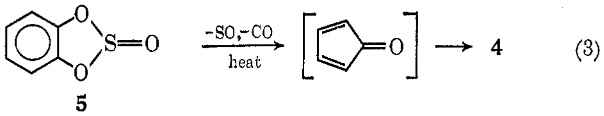
The mass spectra of tetrachloro-*o*-phenylene carbonate (6) and of tetrachloro-*o*-benzoquinone (7) have been compared. The M − CO ion from 6, which is part of a minor fragmentation pathway, may be the same as the molecular ion from 7. The major fragmentation pathway of the molecular ion of 6 involves initial loss of CO_2. When 6 is pyrolyzed in the gas phase by passing it through a heated quartz tube in a stream of nitrogen, products are isolated which can be associated with initial pyrolytic loss of CO_2, and other products can be associated with initial pyrolytic loss of CO. For example, $C_{10}Cl_{10}$, $C_{10}Cl_8$, and C_9Cl_8 compounds have been associated with initial CO_2 loss, whereas tetrachlorobut-1-en-3-yne (11) and dichloro-1,3-dibutadiyne (12) have been associated with initial CO loss. When 7 is pyrolyzed, 11 and 12 are isolated, as well as the dimer of tetrachlorocyclopentadienone; this indicates 7 is the intermediate formed in that pyrolytic pathway of 6 involving initial CO loss. A ketocarbene could be the intermediate formed in that pyrolytic pathway of 6 involving initial CO_2 loss. Thus, these electron-impact and pyrolytic fragmentations appear to be qualitatively similar.

The mass spectra of a number of organic carbonates and cyclic sulfites have been compared with the products isolated from their pyrolyses, and similarities and differences have been noted.[2-6] For example, the mass spectrum of *o*-phenylene carbonate (1) shows the loss of CO_2 followed by CO to be the major fragmentation of the molecular ion; a minor path involves successive losses of CO for a total of 3CO lost.[5] When **1** is pyrolyzed in a stream of nitrogen in the presence of methanol, an intermediate ketene **2** is trapped and isolated as dimers of methyl cyclopentadiene-1-carboxylate (**3**) (44% at 810°) (eq 1).[5] This path is similar to the major fragmentation of the molecular ion of **1**, *i.e.*, CO_2 is initially eliminated. A dimer **4** of cyclopentadienone is also obtained (14% at 810°) *via* a pathway (eq 2) involving loss of 2CO. This path is similar to the minor fragmentation of the molecular ion of **1**, *i.e.*, CO is initially lost.

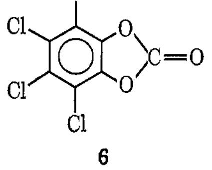


The molecular ion of *o*-phenylene sulfite (**5**) eliminates SO followed by CO. When **5** is pyrolyzed, **4** is isolated in 30% yield (eq 3); cyclopentadienone forms *via* loss of SO followed by CO.[6]

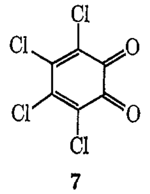




Tetrachloro-*o*-phenylene carbonate (**6**) has been studied with pyrolytic and electron-impact techniques, and we report the results in this article. *o*-Benzoquinone (**7**) has also been studied in order to determine the extent to which it functions as one of the intermediates in the pyrolysis of **6**.



6



7

Experimental Section

Infrared spectra were recorded with a Perkin-Elmer Infracord. Mass spectra were obtained from an Atlas CH4 or an A.E.I. MS 902 mass spectrometer. All glpc work was 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 Tetrachloro-*o*-phenylene Carbonate (6).—Tetrachlorocatechol (Aldrich), 50 g, was added to a solution of 18 g of

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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 from the Ph.D. Dissertations of D. A. Brent and of R. Y. Van Fossen, Wayne State University, Detroit, Mich., 1970. (c) D. A. Brent acknowledges the financial support of the Frank Knoller and Detroit New Research Fellowships.

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

[3] G. G. Smith and B. Koesters, *Chem. Ber.*, **93**, 2400 (1960).

[4] A. David and J. H. Golden, *J. Chem. Soc. B*, 40 (1968).

[5] D. C. DeJongh and D. A. Brent, *J. Org. Chem.*, **35**, 4204 (1970).

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

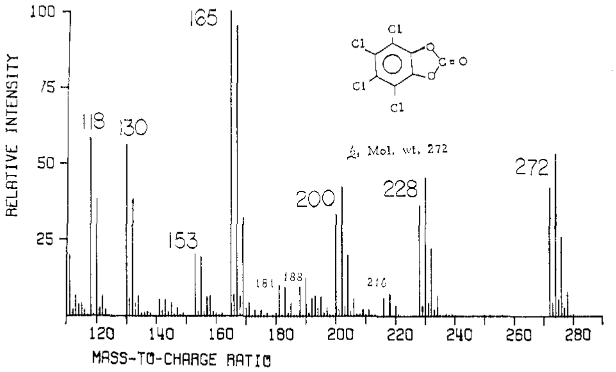

Figure 1.—The 70-eV mass spectrum of tetrachloro-*o*-phenylene carbonate (**6**) (the peak at *m/e* 244 is present in <0.1% relative intensity).

sodium hydroxide in 50 ml of deaerated water (under nitrogen). After the addition of 150 ml of toluene, the solution 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 room temperature. The solution was filtered and the toluene layer was evaporated to dryness. (Unreacted phosgene might still be present in the toluene at this point. Therefore, evaporation was carried out in the hood.) A 31% yield of **6** was obtained: mp 167–168.5° (lit.[7] 172–173°); ir bands 1890, 1850, 1825 cm^{-1}; mass spectrum (70 eV); see Figure 1.

Anal. Calcd for $C_7Cl_4O_3$: C, 30.68; Cl, 51.80. Found: C, 30.98; Cl, 51.56.

Tetrachloro-*o*-benzoquinone (7).—Tetrachloro-*o*-benzoquinone (**7**) was used as purchased (Aldrich) without further purification, mass spectrum (70 eV); see Figure 2.

Preparation of Bis(pentachlorocyclopentadienyl) (8).—Bis(pentachlorocyclopentadienyl) (**8**) was prepared from hexachlorocyclopentadiene (Matheson Coleman and Bell) using the procedure of McBee, Idol, and Roberts:[8] yield, 29%; mp 118–120° (lit.[8] 120–121°); mass spectrum (70 eV) *m/e* (rel intensity) 470 (5), 400 (5.5), 330 (7.5), 295 (2.0), 270 (2.5), 260 (9.3), 235 (100); in each cluster of Cl isotopes, only the relative intensity of the peak of lowest *m/e* is given. The molecular ion is found at *m/e* 470. The relative intensities are somewhat dependent on instrumental parameters. A direct probe was used for sample introduction.

Preparation of Pentachloroanisole (9).—To 6 g of sodium hydroxide in 400 ml of water was added 13 g of pentachlorophenol (Aldrich), followed by 9 ml of dimethyl sulfate. The solution was stirred and warmed; a white precipitate formed which was filtered and washed with small portions of 95% ethanol. The residue was dried and 1 g of **9** was obtained: mp 106–107° (lit.[9] 108–109°); mass spectrum (70 eV) *m/e* (rel intensity) 278 (61), 263 (45.5), 235 (29.5), and clusters corresponding to 5Cl, base peak, *m/e* 280 (100).

Pyrolyses.—The pyrolysis apparatus and procedure for use with a quartz tube heated by an electric furnace have been described in a previous article.[10] In the trapping experiments, the trapping agents were added at the point the stream enters the heated area.

In the alternate pyrolysis apparatus, a heated Nichrome coil is used. The flow of the carrier gas (N_2) is controlled by means of a needle valve, and the nitrogen is dried by passing it through a drying tower containing Drierite. The rate of gas flow is read from a rotometer calibrated in liters/minutes and adjusted by means of a needle valve. The carrier gas is passed through a heated chamber containing the material to be pyrolyzed placed on a porous glass disk. The carrier gas and reactant vapor are passed through a reactor which contains heated, coiled Nichrome wire bent back upon itself to form five or seven strands. The vapors leaving the reactor are led into a series of cooled traps. The pressure of the system is obtained from a McLeod gauge or a manometer. A thermocouple is placed into the center of the coiled strands of wire; the temperature reported for the pyrolysis is obtained from a calibration curve of temperature *vs.* reading on the transformer dial.

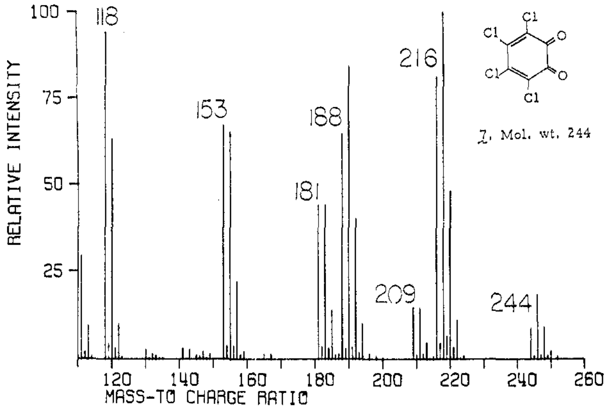

Figure 2.—The 70-eV mass spectrum of tetrachloro-*o*-benzoquinone (**7**).

Pyrolysis of Tetrachloro-*o*-benzoquinone (7). A. Wire.—In a typical experiment, compound **7** (1.21 g) was pyrolyzed over the Nichrome coils at 650°, at a system pressure of 17 mm, and a nitrogen flow rate of 0.50 l./min. A total of 784 mg of crude pyrolysate was obtained. Octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione (**10**) was obtained from the crude pyrolysate in 47% yield: mp 158–160° (lit.[11] 160–161°); ir, same as reported.[12]

B. Oven.—In a typical experiment, compound **7** (1.6 g) was pyrolyzed with the quartz tube heated to 710–720° at a nitrogen flow rate of 0.85 l./min. The products were separated by glpc on a 3 ft × 0.25 in., 5% Apiezon L on Chromosorb W, 60–80 mesh column programmed at 50–225°. Yields were determined by comparing (by weighing) areas of peaks produced by solutions of the pyrolysis products with those of standard solutions. Tetrachlorobut-1-en-3-yne (**11**), 60.2% yield, was identified by its ir spectrum[13] and mass spectrum (70 eV) *m/e* (rel intensity) 188 (76) [190 (100)], 153 (73), 118 (48). Dichloro-1,3-butadiyne (**12**) was obtained in less than 1% yield; it was identified by its ir spectrum[14] and mass spectrum (70 eV) *m/e* (rel intensity) 118 (100), 83 (22). Dimer **10** was obtained in 13.6% yield. A small quantity of a compound was isolated by column chromatography (silica gel) and identified as C_8Cl_8 by mass spectrometry. It is probably a dimer of tetrachlorobut-1-en-3-yne.[13]

When compound **7** (2.0 g) was pyrolyzed at 850° at a nitrogen flow rate of 0.7 l./min, the two major products were **11** and **12**. By relative glpc peak areas, **12** was approximately twice as abundant as **11**. No $C_{10}Cl_{10}$, $C_{10}Cl_8$, or C_9Cl_8 compounds have been isolated from pyrolysis of **7** when either the oven or the wire method was used.

Pyrolysis of Tetrachloro-*o*-phenylene Carbonate (6).—The conditions and results of two pyrolyses of **6** are given in Table I.

Table I

Conditions and Results of Pyrolyses of Tetrachloro-*o*-phenylene Carbonate (6)

Amount of 6	Oven temp, °C	N_2 flow rate	% yields 11	% yields 12
0.985 g	750–760	0.8 l./min	4.6	12.3
0.970 g	700	0.8 l./min	2.8	14.9

None of dimer **10** was obtained. Compounds **11** and **12** were obtained from a trap cooled by 2-propanol–Dry Ice, and they were collected from glpc; yields are given in Table I. The first trap after the oven was air-cooled; a chloroform solution of the

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[7] R. E. Stenseth, R. M. Schisla, and J. W. Baker, *J. Chem. Eng. Data*, **9**, 390 (1964).

[8] E. T. McBee, J. D. Idol, and C. W. Roberts, *J. Amer. Chem. Soc.*, **77**, 4375 (1955).

[9] T. van der Linden, *Recl. Trav. Chim. Pays-Bas*, **57**, 781 (1938).

[10] D. A. Brent, J. D. Hribar, and D. C. DeJongh, *J. Org. Chem.*, **35**, 135 (1970).

[11] M. R. Kamal and J. E. Wicklatz, *Can. J. Chem.*, **42**, 1500 (1964).

[12] "Sadtler Standard IR Spectra," Sadtler Research Laboratories, Philadelphia, Pa., Spectrum No. 23,569.

[13] A. Roedig and R. Kohlhaupt, *Tetrahedron Lett.*, 1107 (1964).

[14] F. Straus, L. Kollek, and H. Hauptmann, *Chem. Ber.*, **63**, 1886 (1930).

material in this trap was placed on a silica gel column. The column was eluted with hexane followed by ether. Nothing was obtained from the ether fractions. Upon evaporating the hexane fractions, a solid remained which moves as one spot on tlc (silica gel) developed with hexane.

The mass spectrum of the brownish-colored solid shows that it is a mixture of $C_{10}C_{10}$, $C_{10}Cl_8$, and C_9Cl_8 compounds: mass spectrum (70 eV) *m/e* (formula, rel intensity) 470 ($C_{10}Cl_{10}$, 3), 400 ($C_{10}Cl_8$, 21), 388 (C_9Cl_8, 0.6), 353 (C_9Cl_7, 6), 235 (C_5Cl_5, 100). The uv spectrum of this mixture is similar to the uv spectrum of octachloronaphthalene (**13**),[15] indicating that the $C_{10}Cl_8$ component is **13**. There are no absorption maxima at 386 or 590 nm in the uv spectrum of the mixture; hence $C_{10}Cl_8$ is not the blue compound octachlorofulvalene.[16]

The colors, uv spectra, and mass spectra of six known $C_{10}Cl_{10}$ isomers with bicyclopentyl carbon skeletons have been reported.[17] The data from our mixture were compared with the data reported for these six isomers and are most consistent with the assignment of the $C_{10}Cl_{10}$ component with the structure bis(pentachlorocyclopentadienyl) (**8**).[18] Attempts to separate the components from the small amount of mixture available were unsuccessful.

In order to get a rough estimation of yields, the $C_{10}Cl_{10}$ component was assumed to be **8** and the $C_{10}Cl_8$ component was assumed to be **13**. The mixture, **8**, and **13** have absorption maxima at 330 nm in their uv spectra. A λ_{max} 275 nm (log ϵ 4.67) has been reported for **13**,[15] and a λ_{max} 280 (log ϵ 3.32) has been reported for **8**;[17] the uv spectrum of the mixture has a maximum at 277 nm. Compounds **8** and **13** were assumed to follow Beer's Law and the method of continuous approximation was employed using the absorbances at 330 and 275 nm in the uv spectrum of the mixture. The yields for **8**, estimated on this basis, were 12.6 and 9.7% for the two pyrolyses, and the yields for **13** plus the C_9Cl_8 component were 9.0 and 7.1% for the two runs.

Trapping of Pyrolytic Intermediates from 6. A. Using Methanol.—Attempts were made to trap intermediates in the pyrolysis of **6** by introducing methanol into the stream before it enters the oven. No trapped intermediates were isolated; oven temperatures of 702–740 and 800–830° were used.

B. Using Dimethyl Acetylenedicarboxylate.—A furnace setting of 800° was used, with a system pressure of 22 mm and a flow rate of 0.9 l./min. The trapping agent required heating to 115–117° in order to volatilize it into the stream at the point it enters the oven area; 10 ml of agent and 1.5 g of **6** were used. No trapped intermediates were isolated, and no trapping agent was recovered.

C. Using Carbon Disulfide.—**6** (1 g) and 25 ml of CS_2 were pyrolyzed as described above: oven, 800–820°; nitrogen flow rate, 0.8 l./min; system pressure, 18 mm. The major product was **11**; minor products were hexachloro-1,3-butadiene (**14**), tetrachlorothiophene (**15**), hexachlorobenzene, and recovered **6**. The mass spectrum of **14** exhibits a molecular ion at *m/e* 258 (with a 6Cl isotope cluster); the ir spectrum of the isolated material agrees with the published spectrum.[19] Tetrachlorothiophene (**15**) was identified by ir[20] and mp 28° (lit.[21] 29°); mass spectrum (70 eV) *m/e* (rel intensity) 222 (100), 220 (M^+, 75.6), 185 (27.2), 150 (9.5), 141 (25.2), and peaks due to Cl isotopes. Hexachlorobenzene and tetrachloro-*o*-phenylene carbonate (**6**) were identified by comparison of their retention times on glpc, ir spectra, and mass spectra with those of authentic samples.

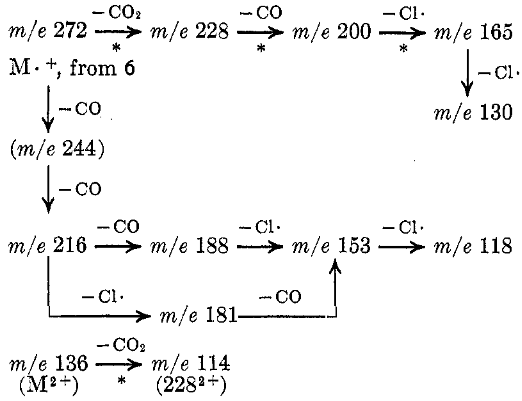
Pyrolysis of Pentachloroanisole (9).—Pentachloroanisole (**9**) (0.5 g) was pyrolyzed with the oven set at 850–880°. No peaks due to $C_{10}Cl_{10}\cdot^+$ are evident in the mass spectra of crude mixtures of products; peaks due to $C_6Cl_6\cdot^+$ and $C_6HCl_5\cdot^+$ are present.

A crystalline product was sublimed from the brown mixture of products at room temperature and atmospheric pressure. The mass spectrum of the compound shows it to be C_6HCl_5. The ir spectrum agrees with that published for pentachlorobenzene.[22]

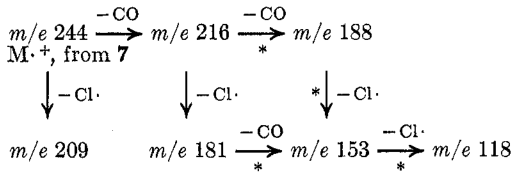
Results

Mass Spectra of Tetrachloro-*o*-phenylene Carbonate (6) and Tetrachloro-*o*-benzoquinone (7).—The 70-eV mass spectrum of **6** is given in Figure 1 and is summarized in Scheme I. The M − CO_2 path is favored over the M − CO path, both in terms of relative intensities of peaks and the presence of metastables. The 70-eV spectrum of **7** is given in Figure 2 and is summarized in Scheme II. The losses of 2Cl in the schemes are shown as stepwise losses of Cl· rather than losses of Cl_2, because metastable peaks are found in the mass spectrum of **7** for the former type of elimination.

SCHEME I



SCHEME II



At lower voltages, the M − CO path in the mass spectrum of **6** becomes of increasingly less importance, whereas the M − CO_2 path remains prominent. For example, at 18 eV (uncorrected) the base peak is *m/e* 274; the prominent fragment ions are *m/e* 228 (27.8%), 200 (19.6%), and 165 (5.6%).

Examination of the two spectra shows that the peaks which are intense in the mass spectrum of **7**, *e.g.*, *m/e* 118, 153, 181, 188, and 216, and their isotope peaks, represent the minor path (M − CO) in the mass spectrum of **6**. Thus an ion corresponding to the molecular ion of **7** may be the intermediate in this minor fragmentation pathway of the molecular ion of **6**.

Pyrolysis of Tetrachloro-*o*-benzoquinone (7).—Tetrachloro-*o*-benzoquinone (**7**) was pyrolyzed in the gas phase. When the heated reactor consists of coiled Nichrome wire heated to 650°, octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione (**10**) is isolated (eq 4). The formation of **10** can be rationalized by the dimerization of tetrachlorocyclopentadienone, formed by the loss of CO from **7**.

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[15] W. L. Mosby, *J. Amer. Chem. Soc.*, **77**, 758 (1955).

[16] V. Mark, *Tetrahedron Lett.*, 333 (1961).

[17] R. M. Smith and R. West, *J. Org. Chem.*, **35**, 2681 (1970).

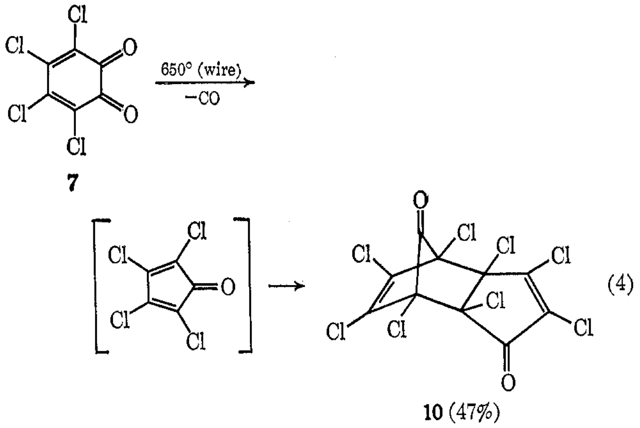
[18] The mass spectrum of **8** has been reported.[17] The peak at *m/e* 470 for the molecular ion is given as <1% relative intensity. We find relatively intense peaks at *m/e* 470 and 235 in the mass spectrum of **8** as well as in the mass spectrum of the mixture. Our spectra were obtained using a direct-introduction probe, whereas the data from Smith and West may have been obtained using a heated-inlet system which increases the possibility of thermal degradation.

[19] Reference 12, Spectrum No. 3229.

[20] Reference 12, Spectrum No. 16,580.

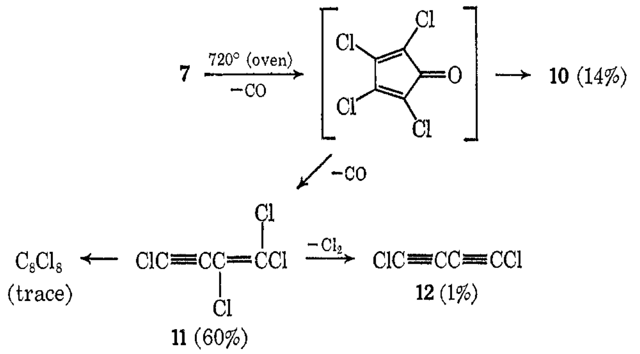
[21] R. C. Weast, Ed., "Handbook of Chemistry of Physics," 49th ed, Chemical Rubber Co., Cleveland, Ohio, 1968.

[22] E. K. Plyer, H. C. Allen, and E. D. Tidwell, *J. Res. Nat. Bur. Stand.*, **58**, 255 (1957).

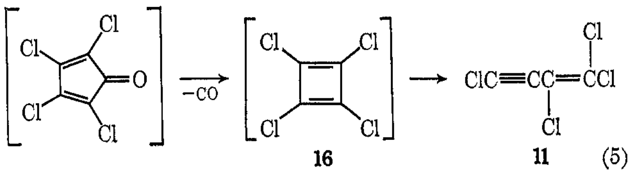


When the heated reactor consists of a quartz tube heated to 720°, the major product from **7** is tetrachlorobut-1-en-3-yne (**11**); **10** is also obtained. Minor quantities of dichloro-1,3-butadiyne (**12**) and of a C_8Cl_8 compound[13] are formed. These results are summarized in Scheme III.

Scheme III



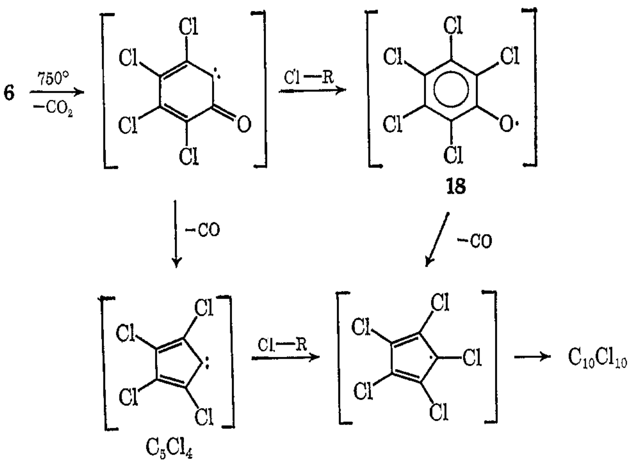
At 850°, **12** is obtained in approximately twice the quantity of **11** and dimer **10** is not formed; thus **11** is probably a precursor of **12**. It is possible that **11** arises *via* a tetrachlorocyclobutadiene intermediate (**16**) (eq 5), although the data do not provide information to confirm this.



Pyrolysis of Tetrachloro-*o*-phenylene Carbonate (6).—When tetrachloro-*o*-phenylene carbonate (**6**) is pyrolyzed, tetrachlorobut-1-en-3-yne (**11**, 12%), dichloro-1,3-butadiyne (**12**, 5%), and a mixture (*ca.* 22%) of $C_{10}Cl_{10}$, $C_{10}Cl_8$, and C_9Cl_8 compounds are obtained. Products **11** and **12** most likely form after initial loss of CO from **6** through the intermediacy of **7** (*cf.* Scheme III). None of dimer **10** was isolated.

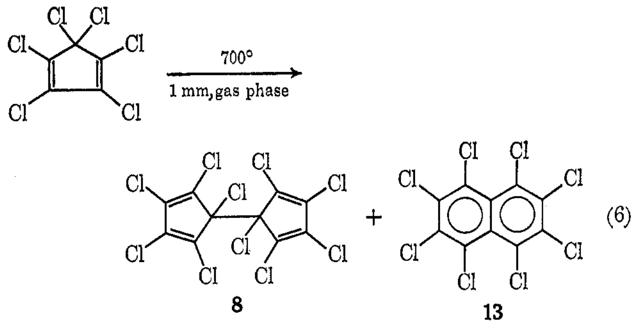
Mass spectral and uv data are most consistent with the assignments of bis(pentachlorocyclopentadienyl) (**8**) to the $C_{10}Cl_{10}$ component and octachloronaphthalene (**13**) to the $C_{10}Cl_8$ component. The C_9Cl_8 component in the mixture is, most likely, octachloroindene (**17**).[23]

Scheme IV



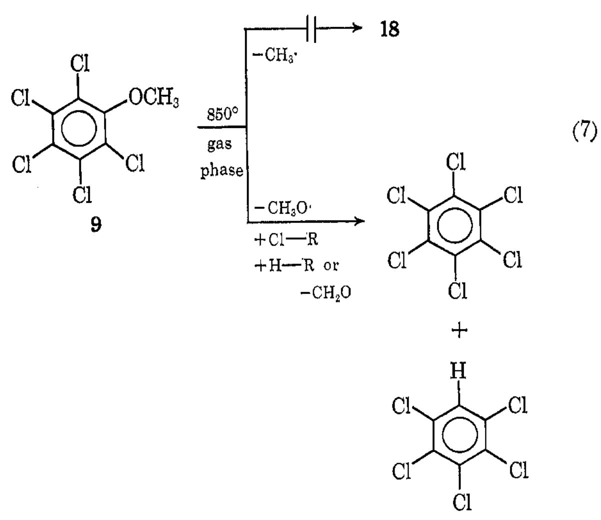
A possible route to $C_{10}Cl_{10}$ is proposed in Scheme IV, in which CO_2 is initially eliminated to form a ketocarbene. The ketocarbene then abstracts a chlorine atom to form intermediate **18** which loses CO; $C_5Cl_5\cdot$ then dimerizes. An alternate route could be formation of a C_5Cl_4 carbene which could abstract a chlorine atom, as shown in Scheme IV also.

Hexachlorocyclopentadiene has been reported to form **8** and **13** upon pyrolysis (eq 6).[24] Thus, it is likely that



8 and **13** arise, at least in part, from an intermediate which is common to the pyrolyses of **6** and of hexachlorocyclopentadiene.

Pentachloroanisole (**9**) was pyrolyzed under the same conditions that **6** was (eq 7), in an attempt to generate



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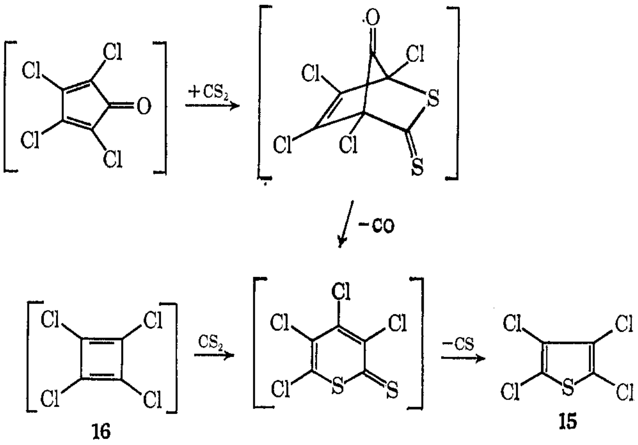
[23] P. Eaton, E. Carlson, P. Lombardo, and P. Yates, *J. Org. Chem.*, **25**, 1225 (1960).

[24] A. E. Ginsberg, R. Paatz, and F. Korte, *Tetrahedron Lett.*, 779 (1962).

intermediate **18** in order to see if it is a precursor to **8**. However, we find that pentachloroanisole cleaves the phenyl–oxygen bond pyrolytically and not the oxygen–methyl bond, and hexa- and pentachlorobenzene are formed. On the other hand, phenyl ethers, including anisole, yield products arising from demethylation as well as demethoxylation.[25–27]

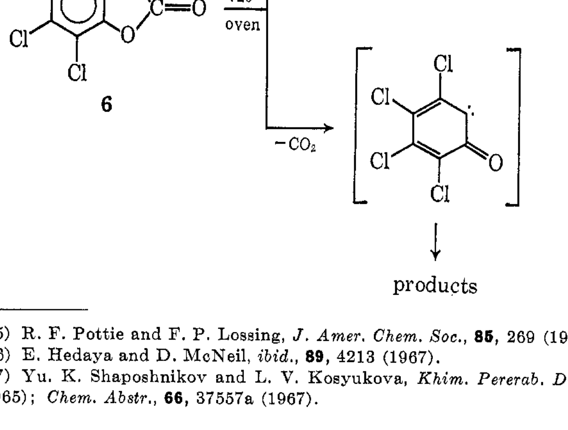
Methanol, CS_2, and dimethyl acetylenedicarboxylate were used in attempts to trap intermediates in the pyrolysis of **6**. No adducts were isolated when methanol and dimethyl acetylenedicarboxylate were used. With CS_2, tetrachlorothiophene (**15**) was isolated. A possible route to its formation from tetrachlorocyclopentadienone is given in Scheme V. It is also possible that CS_2 has trapped **16** or another C_4Cl_4 intermediate.

SCHEME V

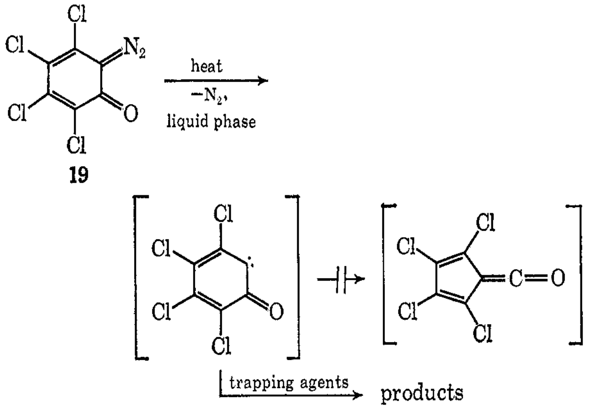


Discussion

The gas phase pyrolysis of tetrachloro-*o*-phenylene carbonate (**6**) can be rationalized by two competing paths, initial loss of CO_2 and initial loss of CO (eq 8). We pyrolyzed tetrachloro-*o*-benzoquinone (**7**) in order to establish that it is an intermediate in the pyrolysis of **6**. The liquid phase pyrolysis of 3,4,5,6-tetrachlorobenzo-2-diazo-1-oxide (**19**) has been reported,[28] and the intermediate suggested in this pyrolysis is the same as that we propose for the loss of CO_2 from **6** (eq 9).

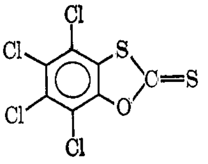


(8)



(9)

The intermediate ketocarbene which forms on the liquid phase pyrolysis and photolysis of **19** does not undergo the Wolff rearrangement to a ketene. It can be trapped with various reagents; for example, trapping with CS_2 yields **20** and with CH_3OH, **21**.[28] However, our gas phase pyrolyses with CS_2, CH_3OH, and dimethyl acetylenedicarboxylate in the stream with **6** did not result in products from trapping, except for a small amount of tetrachlorothiophene (**15**) when CS_2 was used. In the case of dimethyl acetylenedicarboxylate, the trapping agent may have decomposed pyrolytically before it had a chance to react.



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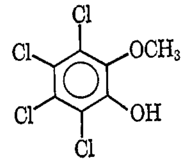

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The $C_{10}Cl_{10}$, $C_{10}Cl_8$, and C_9Cl_8 products, which may be **8**, **13**, and **17**, respectively, can be rationalized most readily in terms of a path involving initial loss of CO_2. On the other hand, formation of tetrachlorobut-1-en-3-yne (**11**) and dichloro-1,3-butadiyne (**12**) can be more readily explained by the route of initial loss of CO from **6**. We pyrolyzed **7** under the same conditions that we had used to pyrolyze **6**; we obtained compounds **11** and **12**. The dimer (**10**) of tetrachlorocyclopentadienone was obtained also, showing that this dienone is also an intermediate in the pyrolysis and has been trapped by dimerization.

A rough estimation of the importance of the M − CO_2 path *vs.* the M − CO in the 70-eV mass spectrum of tetrachloro-*o*-phenylene carbonate can be obtained by summing the relative intensities of peaks associated with each path. Using this approach, the M − CO_2 path is favored over the M − CO path by a factor of 5. By summing the yields of products isolated from the pyrolytic paths associated with the initial loss of CO_2 and with the initial loss of CO, the factor 1.3 is obtained, favoring the M − CO_2 path. Thus, while it is difficult to get accurate quantitative data on the extent to

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which the molecule fragments *via* initial losses of CO_2 and of CO, the electron-impact and pyrolytic fragmentations of **6** appear to be qualitatively similar; the same is true of **7**. We are studying the mass spectra and pyrolyses of various aromatic molecules in order to explore the similarities between the two processes. We hope to develop this technique into a means of predicting a molecule's pyrolysis pathway from its mass spectrum and to elucidate possible electronic relationships between the two processes.

Registry No.—**6,** 711-62-6; **7,** 2435-53-2.

The Pyrolysis of 1,1-Dihexyl-1-methylamine-2-acylimides

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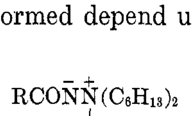
Pyrolysis of 1,1-dihexyl-1-methylamine-2-acetylimide gave 1-hexene, methyl isocyanate, 1-hexyl-1-methyl-2-acetylhydrazine, and dihexylmethylamine. The corresponding benzoyl derivative gave 1-hexene, dihexylmethylamine, diphenylurea, 2-phenylbenzimidazole, benzanilide, and 1-phenyl-3-methylurazole. The abnormal products isolated result from the reaction of phenyl isocyanate with moisture, the aminimide, and 1-hexyl-1-methyl-2-benzoylhydrazine.

Studies of the pyrolysis of open-chain aminimides have been limited to examples containing three methyl groups,[3] two methyls and a 2-acetoxypropyl group,[4] benzyl and two methyls,[5] and recently two methyls and a cyclooctyl or 2-phenylpropyl group.[6] The first two form the tertiary amine and isocyanate and the third type proceeds with rearrangement of the benzyl group. The last two are reported to proceed solely with elimination.

The present work describes the pyrolysis of 1,1-dihexyl-1-methylamine-2-acetylimide (**1a**) and 1,1-dihexyl-1-methylamine-2-benzoylimide (**1b**) and finds that the products formed depend upon the acyl group present.

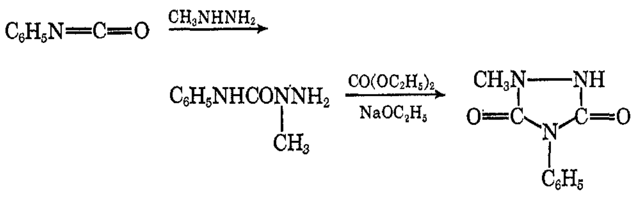


$RCO\overset{-}{N}\overset{+}{N}(C_6H_{13})_2(CH_3)$

1a, R = CH_3
b, R = C_6H_5

1,1-Dihexyl-1-methylamine-2-acetylimide (**1a**) upon pyrolysis at 140° gave 1-hexene, methyl isocyanate, 1-hexyl-1-methyl-2-acetylhydrazine, and dihexylmethylamine. Based on the ratio of the last two compounds, the elimination reaction occurred to the extent of 64.5%.

The 2-benzoyl derivative **1b**, when heated at its decomposition point of 175–185°, gave a more complicated mixture consisting of 1-hexene, dihexylmethylamine, benzanilide, diphenylurea, 2-phenylbenzimidazole, and 1-phenyl-3-methylurazole (**2**). The last compound was identified by comparison with a sample synthesized by the following series of reactions.



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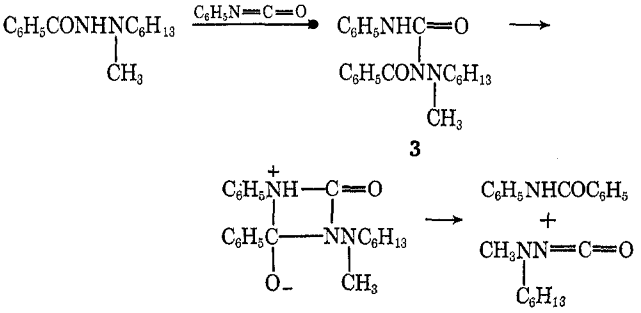
The formation of these products can be rationalized upon the basis of a similar decomposition of the benzoyl derivative **1b** to that found with the acetyl compound **1a**. The absence of phenyl isocyanate or its trimer and 1-hexyl-1-methyl-2-benzoylhydrazine suggests that these compounds are involved in the formation of benzanilide, diphenylurea, 2-phenylbenzimidazole, and 1-phenyl-3-methylurazole (**2**).

2-Phenylbenzimidazole has been isolated previously in the decomposition of 1,1,1-trimethylamine-2-benzoylimide and is considered to be formed from the reaction of phenyl isocyanate with the aminimide.[7]

Diphenylurea is probably formed from phenyl isocyanate and traces of water; no precautions were taken to exclude moisture from the pyrolysis.

Benzanilide and 1-phenyl-3-methylurazole (**2**) result from a reaction of phenyl isocyanate and 1-hexyl-1-methyl-2-benzoylhydrazine. This reaction was verified by heating these two compounds at 170°; 1-hexene, benzanilide, diphenylurea, and 1-phenyl-3-methylurazole were formed.

The initial step in this reaction parallels that observed between phenyl isocyanate and *N*-alkylamides.[8]



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The intermediate urea **3** at the temperature used would decompose into benzanilide and methylhexylaminoisocyanate (**4**). The last species (**4**) is not isolated but reacts with phenyl isocyanate and forms a cyclic amini-

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[1] To whom inquiries should be addressed.

[2] Abstracted in part from the Ph.D. thesis of E. E. Paschke, May 1971.

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