

which possessed absorption at 1725 cm^{-1} in the ir. The nmr spectrum showed that no vinyl hydrogens were present. The two dihydro lumiketones **22** and **23** were separated by preparative gas chromatography using the same procedure described for the lumiketones. A total of 21 mg of **22** and 35 mg of **23** were obtained. See Table I for spectral data.

1,1-Dimethylspiro[4,5]decan-7-one (24).—A mixture of the lumiketones (115 mg) was dissolved in 10 ml of methanol containing 50 mg of 10% palladium on carbon and hydrogenated for 1.0 hr at atmospheric pressure. The catalyst was removed by filtration and the solvent was evaporated at reduced pressure. The resulting oil was taken up in 2.0 ml of benzene and added to a column of silica gel (15 g, $1.75 \times 12.5\text{ cm}$) which was eluted with ten 100-ml aliquots of benzene. Fractions 3–6 were combined to afford 40 mg of the spiro derivative **24**. The structure of this compound is based primarily on the ir spectrum which shows carbonyl absorption at 1720 cm^{-1} and the mass spectrum which has a parent peak at m/e 180. Fractions 11–13 were combined and shown to be the dihydro compound **23** by spectral properties.

Quantum Yield Determination.—The method of Hatchard and Parker²⁸ utilizing potassium ferrioxalate as the actinometer was employed. A Bausch and Lomb Model 33-86-25 ultraviolet grating monochromator equipped with a 200-W super pressure mercury source and power supply was used as a light source for these studies. The quantitative determination of the lumiketones was accomplished using cyclododecane as the internal standard by gas chromatography on a UCW-98 column at 165° .

In a typical experiment, 70.3 mg ($4 \times 10^{-4}\text{ mol}$) of dienone **6** was diluted to 100 ml with spectral grade dioxane in a volumetric flask and irradiated for 120 min at 2537 \AA .

Analysis of Phenols by Gas Chromatography.—Each solution to be analyzed was checked for the presence of dienone **6** either by ir spectroscopy or glc on UCW-98. If present, separation was accomplished by adsorption of the phenols onto basic alumina from an ether solution. The phenols were eluted from the alumina with methanol which was evaporated to dryness and the ether soluble portion of the residue was used. This solution was analyzed on the two columns shown in Table III. The mixture of phenols was then acetylated by heating on a steam

TABLE III

GLC RETENTION TIMES OF PHENOLS AND PHENOL ACETATES

Phenol	Retention times (min)		
	UCW-98 ^a	DC-11 ^b	UCW-98 ^{a,c}
20	20	14	26
25	20	14	24
26	16	10	24
27	18	12	30
28	16	12	24

^a 6-ft UCW-98 on Chromosorb W at 130° at a flow rate of 20 ml/min. ^b 6-ft DC-11 on Chromosorb W (DMCS treated) at 115° at a flow rate of 50 ml/min. ^c Data for phenol acetates, same as in *a* but at 50 ml/min.

bath for 0.5 hr in a solution of 2.0 ml of acetic anhydride and 1.0 ml of pyridine and analyzed as shown in Table III. Since authentic samples of all the phenols and their acetates were on hand it was possible, by coinjection techniques, to identify all five isomeric phenols.

Registry No.—**6**, 20691-79-6; **7**, 20674-83-3; **8**, 20674-14-0; **17**, 26315-95-7; **18**, 26315-96-8; **22**, 20674-15-1; **23**, 26315-98-0; **24**, 26315-99-1; **26**, 26316-00-7; 4-methyl-4-hydroxyphenyl-1-pentanol bisphenylurethane, 26316-01-8; 4,4-dimethyl- α -butyrolactone, 3123-97-5; 4-methyl-*p*-hydroxyphenyl-1-pentanoic acid, 23203-47-6.

Acknowledgment.—The authors are grateful for the support of this investigation by the U. S. Army Research Office (Grant DA-AROD-31-124-G812) and the National Science Foundation (Grant GP-7433). We also gratefully acknowledge the support given to W. V. C. by the American Cyanamid Co. through the award of a research fellowship.

Chlorination of 2-Fluoropropene.

3-Chloro-2-fluoropropene and Some of Its Derivatives

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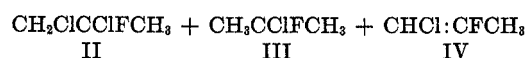
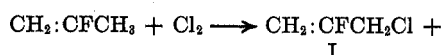
Received May 28, 1970

3-Chloro-2-fluoropropene, a new reactive intermediate, was prepared by chlorination of 2-fluoropropene under a variety of conditions where an ionic mechanism predominated, but not under radical conditions. 3-Amino-2-fluoropropene, 2-fluoro-3-iodopropene, 2-fluoro-2-propenol, and 2-fluoro-2-propenyl ethyl ether were prepared to demonstrate the reactivity. 3-Chloro-2-fluoropropene can be copolymerized to low polymers with acrylonitrile and methyl methacrylate. 3-Chloro-2-fluoropropene and its derivatives are very toxic and should be handled with extreme caution.

It has become evident from the examples which have appeared in the literature¹ that the pathway of chlorination is very much dependent on the conditions which control ionic *vs.* radical reaction. In most cases those molecules of the type $\text{CH}_2\text{CY}=\text{CH}_2$ undergo allylic chlorination under ionic conditions.² The usual examples of compounds which react by allylic chlorination are 2-methylpropene, which yields 3-chloro-2-methylpropene,³⁻⁶ 2-chloropropene, which yields mainly 2,3-di-

chloropropene,⁷⁻⁸ and 2-chlorobutene-2, which yields 2,3-dichlorobutene-1.⁸

The chlorination of 2-fluoropropene under non-free-radical conditions proceeds rapidly to form the new compound 3-chloro-2-fluoropropene (I), 1,2-dichloro-2-fluoropropane (II), 2-chloro-2-fluoropropane (III), and a very small amount of 1-chloro-2-fluoropropene (IV).



(6) A. Streigler, *Chem. Tech. (Berlin)*, **9**, 523 (1957).

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(8) G. W. Hearne (to Shell Development Co.), U. S. Patent 2,290,614 (Sept 22, 1942).

* To whom correspondence should be addressed.

(1) M. L. Poutsma, *Science*, **157**, 997 (1967).

(2) H. P. A. Groll and G. W. Hearne, *Ind. Eng. Chem.*, **31**, 1530 (1939).

(3) W. E. Vaughan and F. F. Rust, *J. Amer. Chem. Soc.*, **61**, 215 (1939).

(4) I. D'yakonov and D. Tishchenko, *J. Gen. Chem. USSR*, **9**, 1258 (1939).

(5) J. Burgin, W. Engs, H. P. A. Groll, and G. W. Hearne, *Ind. Eng. Chem.*, **31**, 1413 (1939).

The reaction is similar to that of 2-chloropropene in most respects, including the nature of products I and II and the ratio in which these are formed. However, vinylic chlorination, which forms a significant amount of 1,2-dichloropropene from 2-chloropropene, does not occur to any appreciable extent with 2-fluoropropene. Also, III, from the addition of hydrogen chloride to 2-fluoropropene, is observed under conditions where hydrogen chloride does not add to 2-chloropropene or 2-chlorobutene-2.

Results

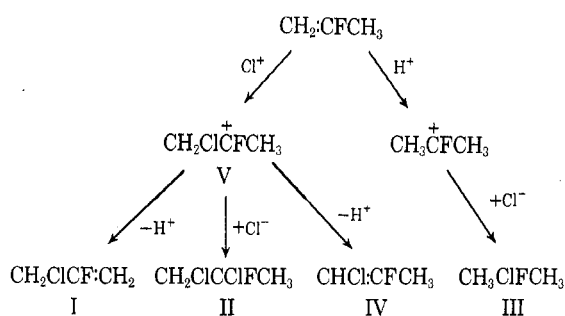
The chlorination of 2-fluoropropene was carried out in a flask using neat liquids at -40 to -50° , in solvent at the same temperature, and in a continuous flow reactor at temperatures ranging from -50 to $+250^\circ$. Yields and efficiencies of up to 67% of I were obtained.

Radical chlorination of 2-fluoropropene was carried out in a U-tube flow system with the light source in the center. There was a steady hot spot in the system indicating a distinctly exothermic reaction and the product was almost exclusively that of chlorine addition, II. This agrees with the known chlorine addition under radical conditions for 2-methylpropene,⁵ 2-chloropropene,⁷ and 2-methacrylonitrile.⁹

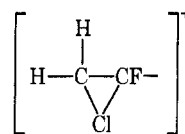
Discussion

Taft¹⁰ has summarized the evidence which excludes radical substitution in the allylic position in such reactions, and Arnold and Lee¹¹ have presented evidence for a cyclic concerted mechanism. The results of our work are in agreement with the fact that allylic substitution is not radical but shed no light on the possibility of the cyclic mechanism. However, the occurrence of vinylic chlorination¹⁻⁷ is evidence against the cyclic concerted mechanism.

The main reaction is pictured as proceeding by the addition of a chloronium ion followed by loss of a proton or addition of chloride. These steps lead to the three



types of compounds also observed when 2-methylpropene and 2-chloropropene are chlorinated. In the chlorination of 2-fluoropropene, IV is detected in only very low yields and therefore the nature of the intermediate V differs from that of the intermediates in the chlorination of 2-methylpropene and 2-chloropropene. Several possible explanations can be considered. (a) The intermediate is in the form of a fluorine containing bridged chloronium ion in which the inductive effect of the fluorine changes the bonding enough to inhibit the loss of a

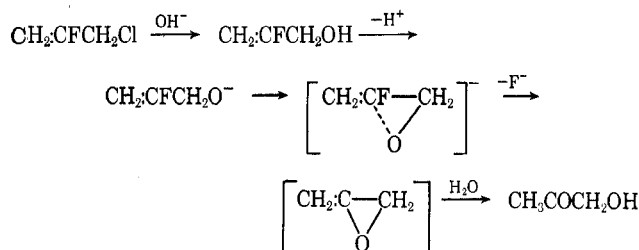


proton from the carbon to which the chlorine is associated. (b) The fluorine present on the carbonium ion stabilizes it so that it is more selective in the secondary reactions which it undergoes than is the corresponding carbonium ion from 2-chloropropene.

The choice of these two explanations cannot be made conclusively on the basis of the present evidence, but the second is favored in light of (1) the stability of fluorine-substituted carbonium ions found by Olah, *et al.*,¹² and (2) following Hammond's postulate,¹³ in the transition state of the addition of Cl^+ or H^+ , bond formation is nearly complete so that the stability of the intermediate ion has a large effect.

The significant effect of substituent fluorine in ionic addition reactions has been previously indicated^{14,15} and is further evidenced by the ready addition of hydrogen fluoride to 2-fluoropropene under ionic conditions.^{16,17}

Reactions of 3-Chloro-2-fluoropropene.—I undergoes reactions expected of allylic halides¹⁸ to produce 2-fluoro-3-iodopropene, 3-amino-2-fluoropropene, and 2-fluoro-2-propenol, as well as the known 2-fluoro-2-propenyl ethyl ether.¹⁹ The iodide was prepared in 54% yield by the use of sodium iodide in acetone, the amine from ammonia in a pressure vessel in 39% yield, and the ether in 25% yield from ethanol and potassium hydroxide. The preparation of 2-fluoro-2-propenol required a longer heating time and gave a lower yield, 47% compared to 90%, than did that of either 2-propenol or 2-methyl-2-propenol from their corresponding chlorides.²⁰ Chloride titration during the preparation of 2-fluoro-2-propenol indicated over 85% reaction. There was also 8% of the fluorine from the starting material present in the water from the reaction. The cause of the low yield and the formation of fluoride ion can be pictured as an elimination of the fluoride by a "neighboring group" effect involving the anionic form of the alcohol.



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(15) The kinetics of the addition of hydrogen fluoride to vinyl fluoride indicate an activation energy of 17 ± 0.3 kcal/mol, corresponding to a facile reaction: L. O. Moore, unpublished results.

(16) P. R. Austin, D. D. Coffman, H. H. Hoehn, and M. S. Raasch, *J. Amer. Chem. Soc.*, **75**, 4834 (1953).

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(18) M. W. Tamele, C. J. Ott, K. E. Marple, and G. W. Hearne, *Ind. Eng. Chem.*, **33**, 115 (1941).

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(20) F. Koehler (to Rohm and Haas Co.), U. S. Patent 2,323,781 (July 6, 1943).

(9) A. F. Ferris and I. G. Marks, *J. Org. Chem.*, **19**, 1971 (1954).

(10) R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **70**, 3364 (1948).

(11) R. T. Arnold and W. W. Lee, *ibid.*, **75**, 5396 (1953).

An alternate explanation involving the addition of hydroxide ion to the double bond of either I or 2-fluoro-2-propenol does not seem likely.²¹ The longer reaction time reflects the lower reactivity also noted for bromo- and chloro-substituted allylic chlorides.²²

I was copolymerized with acrylonitrile and with methyl methacrylate using radical initiators to give copolymers containing 32 and 46% of I. These had reduced viscosities of 0.40 and 0.05. The difficulty inherent in using an allylic monomer has been discussed by Walling²³ so that the observed low molecular weights were expected.

Toxicity.²⁴—The compounds prepared in this study deserve special note as to their toxicity since it is exceptionally high, especially 2-fluoro-2-propenol. It was known that fluoroacetic acid, fluoroacetate derivatives, fluoroethanol, and compounds from which fluoroacetic acid would be formed by biological degradation have high toxicity.²⁵ The toxicity of fluoroallyl alcohol was tested since the fluorine was adjacent to the hydroxyl group, although it was vinylic, and on oxidation could yield fluoroacrylic acid, for which no toxicity data is available, or possibly fluoromalonic acid which is approximately as toxic as fluoroacetic acid.²⁶

2-Fluoro-2-propenol is as toxic as fluoroacetic acid, LD₅₀ 6–10 mg/kg by intravenous injection and 3–4.4 mg/kg by skin penetration. By ingestion the toxicity is 130 mg/kg. This compound has been cited as having the largest known differential toxicity by skin penetration over ingestion.²⁷

By comparison, I, which could be pictured as being easily converted to the alcohol, has an LD₅₀ of 280 mg/kg by ingestion and 200 mg/kg by skin penetration. The toxicities of the other derivatives prepared in this study were not determined. Fluoroallyl chloride and its derivatives should be handled with extreme CAUTION.

Experimental Section

Chlorination of 2-Fluoropropene.—To a 500-ml tinted-glass flask, equipped with an ebullator and a Dry Ice cooled condenser vented to a water scrubber, set in a bath at -50° was charged 56 g of 2-fluoropropene.²⁸ Chlorine, 65.4 g, was added over a 2-hr period through the ebullator. The products were distilled to give 8.8 g of 2-chloro-2-fluoropropane (III) (bp 35° , n_D^{20} 1.3586), 381 g of 3-chloro-2-fluoropropene (I) (bp 55° , n_D^{20} 1.3983), and 24.6 g of 1,2-dichloro-2-fluoropropane (II) (bp 86° , n_D^{20} 1.4110).

(21) J. D. Park, R. J. McMurtry, and J. H. Adams in "Fluorine Chemistry Reviews," Vol. 2, P. Tarrant, Ed., Marcel Dekker, New York, N. Y., 1968, pp 55–75.

(22) L. F. Hatch, L. B. Gordon, and J. J. Russ, *J. Amer. Chem. Soc.*, **70**, 1093 (1948).

(23) C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, pp 175–178.

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(27) H. F. Smyth, Jr., and J. H. Nair, III, *Ind. Eng. Chem.*, **51**, 75A (1959).

(28) 2-Fluoropropene was prepared from an allene-propyne mixture by a method similar to that of Austin.^{15,29} The exception was that a limited amount of HF was fed with the mixture over a chromium catalyst at 300° and the 2-fluoropropene was recovered directly. Separation from 2,2-difluoropropane was accomplished by distillation and excess propyne was removed by scrubbing through a copper-amine solution.

(29) P. R. Austin (to E. I. du Pont de Nemours and Co.), U. S. Patent 2,585,529 (Feb 12, 1952).

The structure of III³⁰ was confirmed by ir, mass, and nmr spectroscopy, and that of II by comparison with a known sample.³¹ I is a new compound and its structure was confirmed by ir, mass, and nmr spectroscopy.

Anal. Calcd for C₃H₄ClF: Cl, 37.52. Found: Cl, 37.54, 37.55.

The chlorination was repeated in a threefold excess by weight of 1,2-dichlorotetrafluoroethane. In the presence of the diluent the efficiency to I was improved both with respect to the two isolated by-products and high boiling residue. The yield of III was very markedly decreased as shown in Table I, runs 2 and 3.

TABLE I
CHLORINATION OF 2-FLUOROPROPENE

Expt no.	Temp, °C	Mole ratio of Org/Cl ₂	Solvent ratio of		Efficiencies, % of organic reacted		
			C ₂ Cl ₄ F ₂ /Org	Batch	I	II	III
1	-20	1.0	0		38.7	9.2	8.7
2	-35	2.0	0		44.0	4.8	11.0
3	-35	1.1	3		63.7	10.0	2.3
				Flow			
4	-50	3.0	2		54.8	4.1	13.9
5	+42	2.4	2		41.4	28.5	3.1
6	+85	2.3	2		60.6	16.0	8.8
7	247	4.0	2		33.6	16.1	2.4
8	247	4.0	0		29.2	16.7	2.9

Chlorination of 2-Fluoropropene, Flow System.—A continuous reactor comprising a brass mixing tee followed by a coil was placed in a bath regulated to the desired temperature.³² The reactants were metered under pressure as liquids and passed through loops to heat or cool them to the desired temperature before mixing. The products were trapped and distilled. The results are given in the last part of Table I.

Careful distillation of the low boiling products from four separate runs gave a small amount of IV, bp 29–29.5°, n_D^{20} 1.3709. The ir is the same as that of the low boiling isomer isolated by Hatch and McDonald,³³ which was assigned a structure with the halogens trans.

Preparation of 2-Fluoro-3-iodopropene.—I, 9.45 g, was refluxed with 20 g of potassium iodide in 200 g of dry acetone for 15 min. After cooling, filtration and distillation gave 10 g of 2-fluoro-3-iodopropene, bp 110–111°, n_D^{20} 1.5272. Ir and mass spectra confirmed the assigned structure.

Anal. Calcd for C₃H₄FI: C, 19.38; H, 2.17. Found: C, 19.41; H, 2.14.

Preparation of 2-Fluoro-2-propenyl Ethyl Ether.—A solution of 50 g of I and 30 g of potassium hydroxide in 73.0 g of ethanol was heated to 65° for 2 hr. Water was added and the mixture was extracted with ether, dried, and distilled to give 26.5 g of 2-fluoro-2-propenyl ethyl ether,¹⁹ bp 77°, n_D^{20} 1.3771.

Anal. Calcd for C₅H₈FO: C, 57.68; H, 8.71. Found: C, 57.56; H, 8.52.

Preparation of 2-Fluoro-2-propenol.—To 159 g of potassium carbonate and 5 g of copper powder in 700 ml of water was added 94.5 g of I at a rate to maintain the reaction temperature at 90°. The addition required 20 hr. Ether extraction followed by drying and distillation gave 36 g of 2-fluoro-2-propenol, bp 52–55° (100 mm), n_D^{20} 1.3892, d_4^{25} 1.5515.

Anal. Calcd for C₃H₄FO: C, 47.38; H, 6.72, MR, 17.13.³⁴ Found: C, 47.23; H, 6.78; MR, 17.06.

A 3,5-dinitrobenzoate ester was made as a derivative, mp 42–44°.

Anal. Calcd for C₁₀H₇FN₂O₆: C, 44.46; H, 2.61; N, 10.37. Found: C, 44.72; H, 2.84; N, 10.98.

(30) A. L. Henne and M. W. Renoll, *J. Amer. Chem. Soc.*, **59**, 2434 (1937).

(31) A. L. Henne and T. P. Waalkes, *ibid.*, **68**, 496 (1946).

(32) A Dry Ice-acetone bath was used for runs at -50° , a water bath for runs at 42 and 80°, and a molten salt bath for those at 247°.

(33) L. F. Hatch and D. W. McDonald, *J. Amer. Chem. Soc.*, **74**, 2911 (1952).

(34) K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

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.

Acknowledgment.—The authors express thanks to C. M. Lovell for assistance with ir spectra, C. B. Strow, Jr., for running and interpreting the nmr spectra, and J. E. Richardson for running and interpreting the mass spectra.

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

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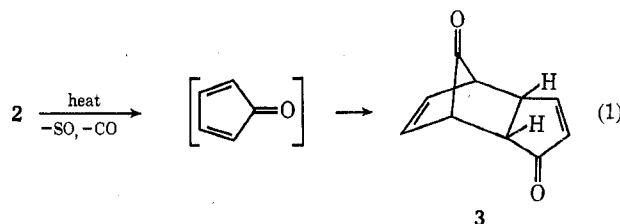
Received June 4, 1970

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.

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