

## Synthesis of Aromatic Polycarbonates by an Anhydrous Catalytic Solution Process. II. The Chloroformate-Chloroformate Interaction

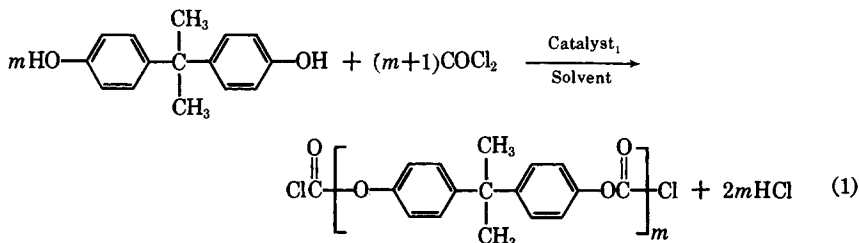
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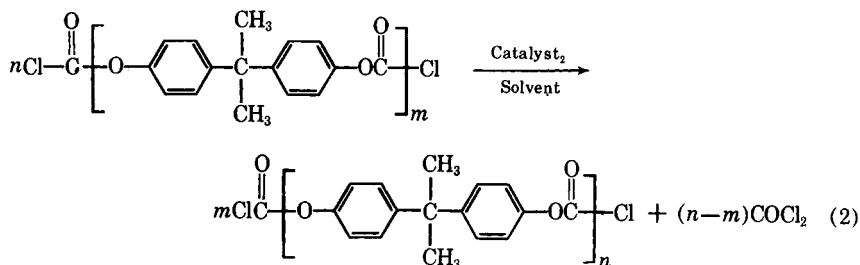
### Synopsis

Several classes of compounds promote the anhydrous condensation of phenyl chloroformate with itself to give diphenyl carbonate and phosgene (or its elements). The compounds in question act either as true catalysts (recoverable unchanged) or as reagents. Salts of magnesium and zinc, particularly the chlorides, belong to the catalytic class. Useful reagents included metal oxides (magnesium, zinc, and calcium) and alkali and alkaline earth metal carbonates, sulfites, bicarbonates, and bisulfites. High molecular weight aromatic polycarbonates were obtained by analogous reactions starting with difunctional chloroformates. Self-condensation of bisphenol-A dichloroformate in the presence of magnesium chloride afforded the polycarbonate with a reduced viscosity 0.2. The use of magnesium oxide allowed the preparation of polycarbonates having reduced viscosities in the useful plastic range (0.45 and higher).

### INTRODUCTION

Three general practical methods<sup>1-3</sup> have been disclosed for the preparation of bisphenol polycarbonates. The first is the aqueous, alkaline direct phosgenation of bisphenols in a heterogeneous system (interfacial polymerization). The second is the direct phosgenation of bisphenols in an inert solvent, in the presence of a stoichiometric amount of a tertiary organic base. The third method involves the ester exchange of the bisphenol with a diaryl carbonate. A fourth possibility is an anhydrous, catalytic process, which may involve several steps or combinations of steps. Some of these were discussed in the first paper of this series.<sup>4</sup> Another route, based on the steps shown in eqs. (1) and (2) for the case of 2,2-bis(*p*-hydroxyphenyl)propane, is the subject of the present paper.





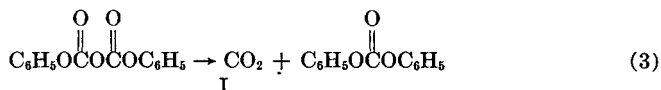
where  $n \gg m$ .

Catalysts for step (1), in which the bisphenol reacts with excess phosgene to afford a chloroformate-terminated prepolymer, were discussed previously.<sup>4</sup> In step (2) the prepolymer is converted to a high polymer by a process which can be considered to be a chloroformate-chloroformate interaction to form a carbonate link and the elements of phosgene. It is apparent that a catalyzed reaction of this type can occur by various combinations of steps, some of which will result in the conversion of phosgene, catalyst, or both to other substances. Therefore, it was to be expected that some of the possible catalysts might also behave as reagents. The initial studies with the proposed catalysts were performed with a model compound, phenyl chloroformate. The results were then applied to the preparation of polymers.

### PRIOR ART

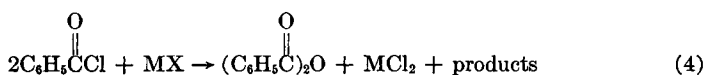
According to Morel,<sup>5</sup> phenyl chloroformate is converted to diphenyl carbonate by boiling with water or aqueous alkali or by reaction with pyridine in ether. A German patent<sup>6</sup> indicated that the latter reaction occurs only on addition of the stoichiometric amount of water. The role of water in this reaction was confirmed in later work<sup>7</sup> with dimethylaniline as the tertiary base.

Chloroformates and acid chlorides give complexes with pyridine.<sup>8,8</sup> The complex from benzoyl chloride<sup>8</sup> decomposes in the presence of water to yield benzoic anhydride. Since the analogous reaction with phenyl chloroformate (*vide ultra*) yields diphenyl carbonate, it is probable that diphenyl pyrocarbonate (I), an analog of benzoic anhydride, is the intermediate:



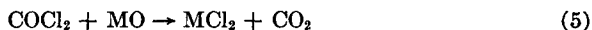
Aliphatic and mixed aliphatic-aromatic pyrocarbonates are known.<sup>9,10</sup> They are stable at lower temperatures but decompose on heating to give carbon dioxide and the corresponding carbonate. No completely aromatic pyrocarbonates have been reported.

It was reasoned that if the pyrocarbonate (I) could be produced in an anhydrous medium from phenyl chloroformate, diphenyl carbonate would be obtained from it as the end-product. The use of similar reaction conditions for the condensation of chloroformate-terminated low or intermediate molecular weight polymer should yield high polymer. An examination of the literature suggested that metal oxides and carbonates might be useful catalysts (or reagents) for this type of reaction. The reaction of benzoyl chloride with metal (mercury, copper, lead) oxides was reported to give benzoic anhydride<sup>11</sup> [eq. (4), X = O]. An analogous reaction with sodium carbonate in the presence of a catalytic amount of pyridine also gave benzoic anhydride, along with carbon dioxide<sup>11</sup> [eq. (4), X = CO<sub>3</sub>].



where M = metal.

Finally, a report by Chauvenet<sup>12</sup> described the high-temperature reaction of phosgene with a variety of metal oxides to give the corresponding chlorides and carbon dioxide:



## EXPERIMENTAL

### Reactions of Phenyl Chloroformate

**Reagents.** Phenyl chloroformate was freshly distilled, b.p. 66°C./9 mm. All inorganic reagents were chemically pure (CP) grade and were thoroughly dried under vacuum with heat before use. Metal oxides were ignited at ~500°C. Solvents were distilled and stored over anhydrous magnesium sulfate. Representative examples of the various reactions are given below.

**Reaction of Phenyl Chloroformate with Magnesium Oxide.** In a round-bottomed 50-ml. flask equipped with a reflux condenser topped by a calcium chloride tube were placed 3.12 g. (0.02 mole) of phenyl chloroformate, 0.4 g. (0.01 mole) of magnesium oxide, and 25 ml. of chlorobenzene. The mixture was heated under reflux for 20 hr., then cooled and filtered to remove the precipitated magnesium chloride. The filtrate was evaporated under vacuum. Crystallization of the residue from *n*-heptane afforded a 96% yield of diphenyl carbonate, m.p. 78–79°C.

It will be seen below (see Results and Discussion) that several classes of compounds were found to promote the reaction of phenyl chloroformate with itself. Some among these acted as reagents, i.e., were taking part in the reaction; magnesium oxide is an example. Others acted as catalysts, i.e., could be recovered unchanged at the end of the reaction. The following example, in which magnesium chloride was used, illustrates such a case.

**Reaction of Phenyl Chloroformate with Magnesium Chloride.** A mixture of 2 g. (0.013 mole) of phenyl chloroformate, 1.2 g. (0.013 mole) of mag-

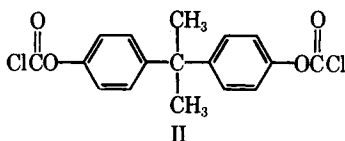
nesium chloride, and 15 ml. of *o*-dichlorobenzene was heated under reflux for 20 hr. Phosgene was evolved rapidly during the first few hours. After cooling, the mixture was filtered and the filtrate distilled under vacuum. Diphenyl carbonate, m.p. 75–77°C., was obtained as the residue in a practically quantitative yield. The recovered magnesium chloride retained its catalytic activity.

Some experiments were conducted in bulk; at the end of the reactions, solvent was added, the solutions were filtered to remove inorganics and worked up in the usual way.

Where conversion to diphenyl carbonate was not quantitative, fractional distillation under vacuum allowed the separation of the unreacted phenyl chloroformate.

### Chloroformate–Chloroformate Coupling in Polymer Systems

All work was carried out with derivatives of 2,2-bis(*p*-hydroxyphenyl)propane, known generically as bisphenol-A. The development of the experimental conditions necessary for production of high polymer was conducted with bisphenol-A dichloroformate (II). This dichloroformate can be regarded as the lowest molecular weight chloroformate-terminated



prepolymer. It was selected because of its availability<sup>13</sup> and ease of handling. The results obtained with II were then applied to chloroformate-terminated prepolymers of low or intermediate molecular weight. Magnesium oxide was the most widely used coupling agent, although a few experiments were also performed with magnesium chloride.

**Reagents.** Bisphenol-A dichloroformate was recrystallized from *n*-hexane, m.p. 94–95°C. Solvents and inorganic reagents were as above. The chloroformate-terminated prepolymers were prepared by the aluminum chloride-catalyzed reaction of bisphenol-A with excess of phosgene in chlorobenzene (133°C.).<sup>4</sup> Procedure B<sup>4</sup> was used in all cases.

This procedure was described in detail in the preceding paper of this series.<sup>4</sup> The prepolymers were isolated by evaporation of the solvent and used as such in the coupling reaction. However, an aliquot sample of the reaction solution was also coagulated in isopropanol. The reduced viscosity of the polymer (initial RV) was determined. Comparison of the latter with the reduced viscosity obtained on the polymer resulting from the coupling step (final RV) was used to assess the success of the prepolymer → polymer conversion.

**Endgroup Analysis on the Prepolymers.** The molecular weight of the prepolymers was determined by cryoscopy. Their hydrolyzable chlorine content was also determined and compared with the one calculated from

their molecular weight. Use of a 20–40% excess of phosgene gave complete chloroformate termination with no detectable chloroformate–solvent interaction.<sup>4</sup> Lower excesses of phosgene led to prepolymers possessing lower than expected hydrolyzable chlorine contents. No high polymers could be obtained from the latter by the chloroformate–chloroformate coupling reaction.

**Reduced Viscosities.** All reduced viscosities were measured at 25°C. in methylene chloride at a concentration of 0.2 g./100 ml.

Two representative experiments with magnesium oxide are presented.

**Reaction of Bisphenol-A Dichloroformate with an Equivalent Amount of Magnesium Oxide.** A mixture of 3.0 g. (0.0085 mole) of bisphenol-A dichloroformate, 0.35 g. (0.0085 mole) of magnesium oxide, and 15 ml. of *o*-dichlorobenzene was heated under reflux in a current of dry nitrogen for 24 hr. The cooled reaction mixture was filtered, and the polymer was precipitated by addition of the filtrate to 150 ml. of isopropanol. The yield was 93%, and the reduced viscosity 0.23.

**Reaction of Bisphenol-A Dichloroformate with Excess Magnesium Oxide.** A mixture of 2.5 g. (0.0071 mole) of bisphenol-A dichloroformate, 2.1 g. (0.050 mole) of magnesium oxide, and 5 ml. of *o*-dichlorobenzene was heated in an oil bath maintained at 190°C. for 3 hr. Carbon dioxide was evolved. The cooled, colorless mixture was diluted with 30 ml. of methylene chloride, stirred for 5 hr. at room temperature and filtered to remove inorganic substances and a small amount of insoluble gel. Addition of the filtrate to about 350 ml. of isopropanol gave a 70% yield of white, fibrous polymer, reduced viscosity 0.71. The infrared spectrum of the polymer was identical to that of an authentic sample of bisphenol-A polycarbonate.

**Reaction of Chloroformate-Terminated Prepolymer with Excess Magnesium Oxide.** By using the technique of the preceding example with 2.5 g. of a prepolymer (initial RV = 0.05) and 2.1 g. (0.050 mole) of magnesium oxide, a polycarbonate with a final RV = 0.58 was obtained in a 92% yield.

## RESULTS AND DISCUSSION

### General

Several classes of compounds were found to promote the coupling of phenyl chloroformate to give diphenyl carbonate and phosgene\* (or its elements). Depending on whether the inorganic coupling agent remains unchanged or takes part in the reaction, the compounds might be classified as catalysts or reagents. However, a classification of this type might sometimes be superficial. Magnesium chloride and magnesium oxide are an illustration. The reaction of phenyl chloroformate with magnesium oxide yields diphenyl carbonate, carbon dioxide, and magnesium chloride. In the presence of magnesium chloride and at elevated temperatures,

\* It was found that phenyl chloroformate (neat) is stable at reflux (180°C.), contrary to the report of Bowden.<sup>14</sup>

diphenyl carbonate and phosgene are obtained from phenyl chloroformate, while the metal chloride remains unchanged. It is possible that the nature of the process is the same in both cases. Phosgene and diphenyl carbonate might be the primary products in the magnesium oxide reaction as well, the metal chloride and carbon dioxide being formed in a secondary reaction of the oxide with phosgene.<sup>12</sup>

Zinc chloride, magnesium chloride, the double salt of magnesium chloride and tetramethylammonium chloride,<sup>4</sup> and magnesium sulfate acted as true catalysts for the reaction of phenyl chloroformate with itself. Metal (zinc, magnesium, and calcium) oxides, alkali and alkaline earth metal carbonates, bicarbonates, sulfites, and bisulfites also promoted the same reaction but took part in it. Therefore, these are reagents.

### Model Reactions with Phenyl Chloroformate

**Catalytic Reactions.** The reaction of phenyl chloroformate with various catalysts (1 mole/mole of phenyl chloroformate) are summarized in Table I. The catalytic nature of the reactions was demonstrated by reusing two

TABLE I  
Reaction of Phenyl Chloroformate with Itself in the Presence of Various Catalysts

Catalyst	Solvent	Time, hr.	Tempera- ture, °C.	Color of crude product	Recrystallized diphenyl carbonate	
					Yield, %	M.P., °C.
ZnCl <sub>2</sub>	None	20	181	Brown	30	75-78
MgCl <sub>2</sub>	None	20	180	White	94	75.5-78
MgCl <sub>2</sub>	<i>o</i> -Dichloro- benzene <sup>a</sup>	20	180	White	95	77-79
MgSO <sub>4</sub>	None	20	180	Slightly yellow	11	72-77
MgCl <sub>2</sub> ·N(CH <sub>3</sub> ) <sub>4</sub> Cl	None	20	180	Brown	73.5	76.5-78.5

<sup>a</sup> 1150 ml./mole of phenyl chloroformate.

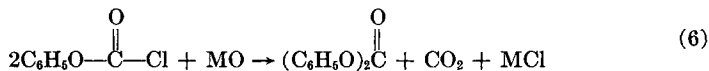
of the catalysts (magnesium chloride and zinc chloride) in other runs which gave results similar to those obtained with the fresh catalysts. No attempts were made to determine the yields of phosgene, but its formation was readily detected.

In a single attempt,  $\alpha$ -naphthyl chloroformate was converted to the corresponding carbonate in an 85% yield by treatment with magnesium chloride under similar conditions.

The mechanism of catalysis is unknown. The possibility that the reaction was promoted by the mere presence of a surface was ruled out by experiments in which treatment of phenyl chloroformate with sodium chloride, lithium chloride, or ground glass gave only unchanged starting material.

### With Reagents

**Metal Oxides.** The reaction between phenyl chloroformate and a metal oxide is shown in eq. (6).



where M = Zn, Mg, Ca.

Results are shown in Table II. Zinc oxide gave high yields of diphenyl carbonate both in bulk and in solution, although products of better color

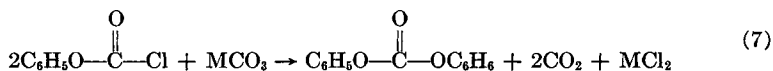
TABLE II  
Reaction of Phenyl Chloroformate with Metal Oxides

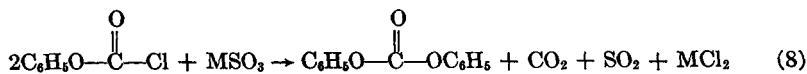
Phenyl chloroformate, moles	Equivalents of metal oxide	Solvent and volume, ml.	Temperature, °C.	Time, hr.	Color of crude product	Recrystallized diphenyl carbonate	
						Yield, %	M.P., °C.
1.0	ZnO, 1.0	None	170	18	Brown	94	77-78
1.0	ZnO, 0.5	None	170	16	Brown	45	77-79
1.0	ZnO, 1.0	Chlorobenzene, 750	133	22	White	38	77-79
1.0	ZnO, 1.0	<i>s</i> -Tetrachloroethane, 750	146	22	White	67.5	76-78
1.0	ZnO, 1.0	<i>o</i> -Dichlorobenzene, 750	180	22.5	White	96	76-78
1.0	MgO, 1.0	None	180	24	White	94	78-79
1.0	MgO, 1.0	Chlorobenzene, 750	133	20	White	96	78-79
1.0	CaO, 1.0	None	180	20	Brown	10	77-78.5
1.0	CaO, 1.0	Chlorobenzene, 750	133	20	—	—	—

and higher purity were obtained when solvents (chlorobenzene, *o*-dichlorobenzene) were used. Magnesium oxide, however, was superior to zinc oxide in all respects: reaction rate, conversion, purity, and color. On the other hand, calcium oxide gave very low reaction rates and low yields of diphenyl carbonate. The large difference in reactivity between these two alkaline earth metal oxides cannot presently be explained.

Rate studies made on solvent-free systems with zinc oxide (by quantitative measurements of carbon dioxide evolution) proved the reaction to be very fast. The technique was the same as that used by Cantwell and Brown in their acid-decarboxylation studies.<sup>15</sup> Representative kinetic runs are shown in Figure 1.

**Metal Carbonates and Sulfites.** The reactions of phenyl chloroformate with metal carbonates and with metal sulfites are represented by eqs. (7) and (8):





Results are summarized in Table III. From the data, it is clear that reaction (7) is strongly catalyzed by pyridine; presumably activation of the phenyl chloroformate is required to permit rapid reaction with the weakly nucleophilic carbonate ion. Catalytic amounts of the tertiary base are adequate, undoubtedly because the free base is regenerated from its hydrochloride by reaction with the metal carbonate.

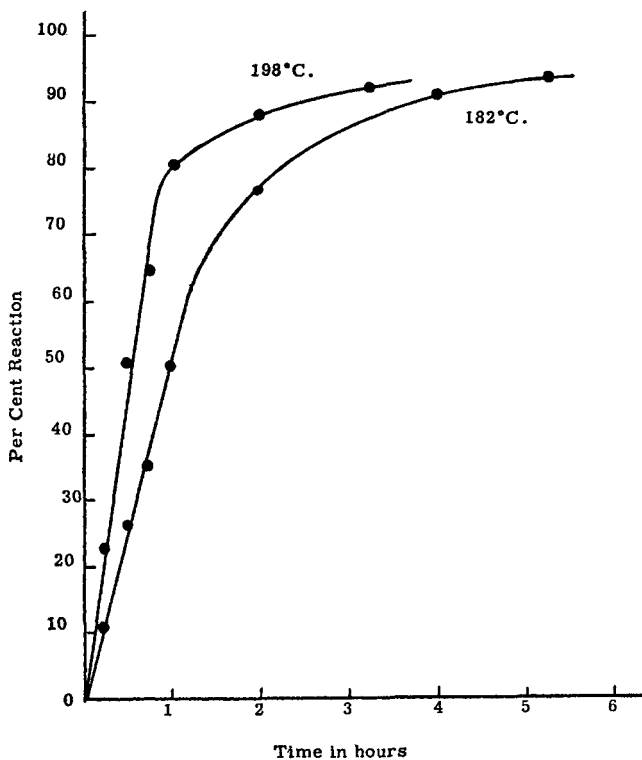


Fig. 1. Reaction of phenyl chloroformate with zinc oxide.

The reaction of sodium sulfite with pyridine gave diphenyl carbonate in 70% yield. No attempt was made to detect diphenyl sulfite, a possible by-product. It is striking that a higher yield of diphenyl carbonate was obtained from sodium sulfite than from sodium carbonate.

**Metal Bicarbonates and Bisulfites.** The reaction of phenyl chloroformate with sodium bicarbonate and a catalytic amount of pyridine (20 hr. in *o*-dichlorobenzene under reflux) gave diphenyl carbonate in 30% yield. With sodium bisulfite, the yield was much higher (97%).

**Mechanism.** No effort was made to elucidate the mechanism of any of these reactions. It is apparent that they are probably very similar. It



TABLE III  
Reaction of Phenyl Chloroformate with Metal Carbonates and Sulfites<sup>a</sup>

Metal carbonate or sulfite	Solvent	Temperature, °C.	Time, hr.	Color of crude product	Recrystallized diphenyl carbonate	
					Yield, %	M.P., °C.
Na <sub>2</sub> CO <sub>3</sub> <sup>b</sup>	None	180	20.5	Slightly brown	3	75-78
Na <sub>2</sub> CO <sub>3</sub> <sup>b</sup>	<i>o</i> -Dichlorobenzene <sup>a</sup>	180	20.5	Brown	3	76.5-78
Na <sub>2</sub> CO <sub>3</sub> <sup>c</sup>	None	180	20.5	Brown	50	77-79
Na <sub>2</sub> CO <sub>3</sub> <sup>c</sup>	<i>o</i> -Dichlorobenzene <sup>a</sup>	180	20.5	Brown	38	77-79
MgCO <sub>3</sub> <sup>c</sup>	None	180	20	White	98	74-78
Na <sub>2</sub> SO <sub>3</sub> <sup>c,d</sup>	None	180	20	Yellow	70	76-78

<sup>a</sup> Phenyl chloroformate (1 mole) was reacted with 0.5 mole of the carbonate or sulfite. The amount of solvent (where used) was 750 ml.

<sup>b</sup> No tertiary base was used in these experiments.

<sup>c</sup> Pyridine (~1-wt. % based on the chloroformate) was used as the catalyst.

<sup>d</sup> The process appeared to be more complicated than as outlined in eq. (8) because some phosgene was also evolved from the reaction medium.

should be pointed out, however, that the diphenyl pyrocarbonate (I) need not necessarily be an intermediate.

### Chloroformate-Chloroformate Coupling in Polymer Systems

The greater part of this work was conducted on bisphenol-A dichloroformate, which can be regarded as the prepolymer of lowest molecular weight [eqs. (1) and (2),  $m = 1$ ]. Representative experiments illustrating its conversion to high polymer by treatment with magnesium oxide are shown in Table IV.

In general, the use of equivalent amounts of magnesium oxide gave

TABLE IV  
Reaction of Bisphenol-A Dichloroformate with Magnesium Oxide<sup>a</sup>

MgO, mole	Solvent and volume, ml.	Time, hr.	Temperature, °C.	Coagulated polymer		
				Color	Yield, %	RV
1	<i>o</i> -Dichlorobenzene, 1500	24	180	White	55	0.14
1	1,2,4-Trichlorobenzene, 1500	24	213	Yellow	88	0.33
10	<i>o</i> -Dichlorobenzene, 1500	3	180	White	70	0.71 <sup>b</sup>
30	1,2,4-Trichlorobenzene, 2000	3	213	White	30	1.02 <sup>b</sup>
30	1,2,4-Trichlorobenzene, 1000	3	213	White	51	0.21 <sup>b</sup>

<sup>a</sup> Reactants: bisphenol-A dichloroformate (1 mole) + magnesium oxide + solvent.

<sup>b</sup> Variable amounts of gelled material were also obtained in these experiments.

only comparatively low polymer, a large excess of the oxide being required to give products of useful molecular weight ( $RV \geq 0.45$ ).

Even when excess magnesium oxide was used, the results were difficult to reproduce. Experiments intended as duplicates often gave discrepancies in the yields and reduced viscosities of soluble polymer and in the yields of insoluble gel. The reasons for this are not completely understood, but apparently do not involve the effect of trace quantities of moisture, since reproducibility was not improved by working in a dry-box. This lack of reproducibility made it necessary to perform several experiments at each set of conditions and to use average results in studying the effect of the recognized variables, which included temperature, concentration, time, and agitation.

The molecular weight of the soluble polymer could be increased by raising the reaction temperature or by working in more dilute solutions. Under favorable conditions (Table IV), products of high molecular weight could be obtained within 3 hr. at  $180^{\circ}\text{C}$ ., longer reaction times giving increased amounts of gel. On the other hand, vigorous stirring reduced the amount of gel with an accompanying decrease in the molecular weight of the soluble polymer.

The origin of the gel is unknown. It is possible that reactions similar to those discussed by Schnell<sup>1,2</sup> are responsible for its formation.

The use of chloroformate-terminated prepolymers of low and medium molecular weights<sup>4</sup> in this magnesium oxide coupling reaction gave results similar to those obtained with bisphenol-A dichloroformate.

Rather surprisingly, all attempts to convert bisphenol-A dichloroformate to high polymers by treatment with catalysts were unsuccessful. In the best run (9 moles of magnesium chloride/mole dichloroformate, 20 hr. in *o*-dichlorobenzene under reflux) the reduced viscosity of the polymer was only 0.20.

## CONCLUSIONS

Several classes of compounds were found to promote the interaction of phenyl chloroformate with itself to give diphenyl carbonate and phosgene (or its elements). These reactions gave high yields of pure diphenyl carbonate. Some of these reagents (magnesium oxide) allowed the preparation of high polymers from difunctional aromatic chloroformates, including chloroformate-terminated carbonate prepolymers. However, the polymer-forming reactions were not always reproducible. Therefore, the catalytic solution process for the preparation of bisphenol-A polycarbonate described in the preceding paper<sup>4</sup> is the preferred modification.

## References

1. Schnell, H., *Angew. Chem.*, **68**, 633 (1956).
2. Schnell, H., *Ind. Eng. Chem.*, **51**, 157 (1959).
3. Schnell, H., L. Bottenbruch, and H. Krimm (to Farbenfabriken Bayer, A.-G.), U. S. Pat. 3,028,365 (1962).

4. Matzner, M., R. P. Kurkijy, and R. J. Cotter, *J. Appl. Polymer Sci.*, **9**, 3295 (1965).
5. Morel, A., *Bull. Soc. Chim. France* [3], **21**, 823 (1899).
6. Bayer, F., and Co., German Pat. 118,566 (1901); *Freidländer*, **6**, 1163.
7. Rivier, H., and P. Richard, *Helv. Chim. Acta*, **8**, 490 (1925).
8. Einhorn, A., and F. Hollandt, *Ann.*, **301**, 95 (1898).
9. Kovalenko, V. I., *Zh. Obshchei Khim.*, **22**, 1546 (1952).
10. Thoma, W., and H. Rinke, *Ann.*, **624**, 30 (1959).
11. Deninger, A., *J. Prakt. Chem.* [2], **50**, 479 (1894).
12. Chauvenet, E., *Compt. Rend.*, **147**, 1046 (1908); *ibid.*, **152**, 87 (1911).
13. Cotter, R. J., M. Matzner, and R. P. Kurkijy, *Chem. Ind. (London)*, **1965**, 791.
14. Bowden, S. T., *J. Chem. Soc.*, **1939**, 310.
15. Cantwell, N. H., and E. V. Brown, *J. Am. Chem. Soc.*, **74**, 5967 (1952).

### Résumé

De nombreuses classes de composés facilitent la condensation en milieu anhydre du chloroformiate de phényle avec lui-même pour former le carbonate de diphényle et le phosgène (ou ses éléments). Les composés en question agissent soit comme vrais catalyseurs (récupérables inchangés), soit comme réactifs. Les sels de magnésium et de zinc, surtout les chlorures, appartiennent à la classe des catalyseurs. Parmi les réactifs, on range les oxydes métalliques (magnésium, zinc, et calcium), les carbonates, bicarbonates, et bisulfates de métaux alcalins et alcalino-terreux. On a obtenu des polycarbonates aromatiques de poids moléculaire élevé par des réactions analogues au départ de chloroformiates bifonctionnels. La condensation du dichloroformiate de bisphénol-A avec lui-même en présence de chlorure de magnésium fournit un polycarbonate avec une viscosité réduite de 0.2. L'utilisation d'oxyde de magnésium permet la préparation de polycarbonates ayant des viscosités réduites adaptées à des usages comme matières plastiques (0.45 et plus).

### Zusammenfassung

Einige Verbindungsklassen begünstigen die wasserfreie Selbstkondensation von Phenylchloroformiat unter Bildung von Diphenylkarbonat und Phosgen (oder seinen Elementen). Die betreffenden Verbindungen wirken entweder als wahre Katalysatoren (unverändert rückgewinnbar) oder als Reaktionsteilnehmer. Magnesium- und Zinksalze, besonders die Chloride, gehören zur katalytischen Klasse. Brauchbare Reaktionsteilnehmer sind Metalloxyde (Magnesium, Zink, und Kalzium) sowie Alkali- und Erdalkalimetallkarbonate -sulfite, -bikarbonate, und -bisulfite. Hochmolekulare aromatische Polykarbonate wurden durch analoge Reaktionen mit difunktionellen Chloroformiaten als Ausgangsprodukten erhalten. Die Selbstkondensation von Bisphenol-A-dichloroformiat in Gegenwart von Magnesiumchlorid lieferte ein Polykarbonat mit einer reduzierten Viskosität von 0.2. Die Verwendung von Magnesiumoxyd erlaubte die Darstellung von Polykarbonaten mit einer reduzierten Viskosität in einem für plastische Massen brauchbaren Bereich (0.45 und höher).

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