Halophenyl and 8-Quinolyl Carbonates

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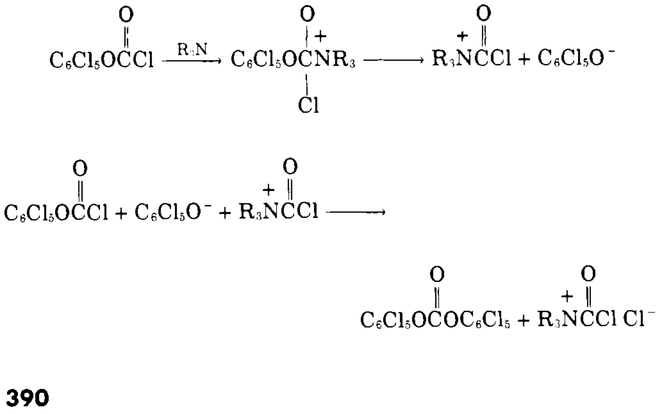
A number of pentahalophenyl, halophenyl, 8-quinolyl, bis(halophenyl), and bis(8-quinolyl) carbonates and dicarbonates of dihydric phenols have been prepared. These compounds were generally synthesized by treating an alkyl or aryl chloroformate with a phenol or alcohol in the presence of a hydrogen chloride acceptor. Infrared measurements were made on representative members of each type. The carbonyl absorptions varied between 1745 and 1800 cm.$^{-1}$ depending on the substituents. Mechanisms have been proposed to explain the formation of bis(pentachlorophenyl) carbonate as a by-product of reactions utilizing pentachlorophenyl chloroformate in the presence of tertiary amines and the formation of bis[2-(diethylamino)ethyl] carbonate during the attempted preparation of 2-(diethylamino)ethyl pentachlorophenyl carbonate from 2-(diethylamino)ethanol and pentachlorophenyl chloroformate.

AS PART OF AN investigation into the preparation of compounds possessing antibacterial activity, a large number of organic carbonates were synthesized. The type of carbonates prepared included pentahalophenyl, halophenyl, 8-quinolyl, bis(halophenyl), and bis(8-quinolyl) carbonates and dicarbonates of dihydric phenols.

In general, these compounds were prepared by treating an alkyl or aryl chloroformate with a phenol or alcohol in the presence of a hydrogen chloride acceptor, such as triethylamine or pyridine. In some instances, pyridine was used as the solvent. In one case (compound 3, Table I), the sodium salt of a phenol was allowed to react with an alkyl chloroformate, and in another (compound 15, Table I), an alcohol and an aryl chloroformate were heated in a high boiling solvent in the absence of a hydrogen chloride acceptor.

Considerable difficulty was experienced in carrying out the reaction of pentachlorophenyl chloroformate with alcohols or phenols in the presence of a hydrogen chloride acceptor due to the formation of bis(pentachlorophenyl) carbonate as a major product. Although we encountered no difficulty in this respect when preparing carbonates from 2,4,5-trichlorophenyl and other aryl and alkyl chloroformates, it has been reported that phenyl chloroformate, in the presence of pyridine, is converted into diphenyl carbonate (*10*). In that instance the formation of an unstable pyridine-phosgene complex along with the bis-carbonate was postulated, but no explanation for the formation of the products was suggested.

The following mechanism is proposed to explain the formation of bis(pentachlorophenyl) carbonate as a by-product in the synthesis of pentachlorophenyl carbonates.



$$C_6Cl_5O\overset{\overset{O}{\|}}{C}Cl \xrightarrow{R_3N} C_6Cl_5O\underset{\underset{Cl}{|}}{\overset{\overset{O}{|+}}{C}}NR_3 \longrightarrow R_3\overset{+}{N}\overset{\overset{O}{\|}}{C}Cl + C_6Cl_5O^-$$

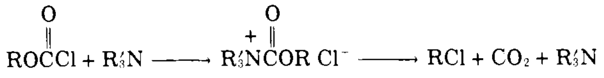
$$C_6Cl_5O\overset{\overset{O}{\|}}{C}Cl + C_6Cl_5O^- + R_3\overset{+}{N}\overset{\overset{O}{\|}}{C}Cl \longrightarrow C_6Cl_5O\overset{\overset{O}{\|}}{C}OC_6Cl_5 + R_3\overset{+}{N}\overset{\overset{O}{\|}}{C}Cl\ Cl^-$$

In this mechanism, the tertiary amine attacks the carbonyl group to form an intermediate from which the pentachlorophenate anion is eliminated. This step may proceed through a long-bonded transition state because of steric factors. The eliminated anion then attacks additional chloroformate to form the bis-carbonate in the normal manner. This side reaction is facilitated in part by the nucleophilicity of the pentachlorophenate anion and more so by the insolubility of the bis-carbonate in the solvents employed for the reaction.

This mechanism is consistent with separate experiments in which pentachlorophenyl chloroformate was dissolved in ether and treated with triethylamine. For each mole of amine used, one mole of bis-carbonate and one mole of $(CH_3CH_2)_3\overset{+}{N}COCl\ Cl^-$ were obtained as a mixture having the correct elemental analysis. Treatment with water yielded the pure bis-carbonate.

A number of variations in the preparative methods were examined in order to retard formation of the undesired bis-carbonate. The extent of its formation was somewhat reduced by carrying out the addition of reactants at 30° or less and by using a weak base as the hydrogen chloride acceptor. An attempt to use Amberlite IR 45, a weakly basic anion exchange resin, as the acid acceptor was unsuccessful; unchanged starting material was recovered.

Low reaction temperatures also hindered formation of by-products when carbonates were prepared from alkyl chloroformates in the presence of tertiary amines. When triethylamine is heated in benzene with an aklyl chloroformate, the amine is cleaved and an alkyl chloride and a carbamate are formed (*3*). Pyridine or quinoline combine with the chloroformate to form an intermediate which decomposes into an alkyl chloride and carbon dioxide (*5, 7*). .



$$RO\overset{\overset{O}{\|}}{C}Cl + R_3'N \longrightarrow R_3'\overset{+}{N}\overset{\overset{O}{\|}}{C}OR\ Cl^- \longrightarrow RCl + CO_2 + R_3'N$$

For those compounds prepared from alkyl chloroformates using pyridine as both the solvent and acid acceptor, it was necessary to operate at ice-bath temperatures in order to retard decomposition of the pyridine-alkyl chloroformate intermediates to alkyl halides. This method failed for methyl 8-quinolyl carbonate because of an unusually rapid decomposition of the intermediate; however, this carbonate was prepared in good yield by using equivalent amounts of pyridine and chloroformate and using ether as the solvent.

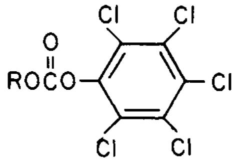
Similarly, benzyl aryl carbonates could not be obtained using an organic base as an acid acceptor due to rapid decomposition of the intermediate to benzyl chloride and carbon dioxide. Instead, an aqueous solution of sodium hydroxide was added to a heterogeneous system composed of the alcohol, chloroformate, sodium carbonate, and benzene.

In the preparation of several 2-chloroethyl carbonates using pyridine as the solvent, it was necessary to remove excess pyridine at low temperature and reduced pressure in order to minimize quaternary salt formation between pyridine and the 2-chloroethyl group (method 11).

When p-chlorophenyl 8-quinolyl carbonate was prepared, the reaction mixture was hydrolyzed with sodium acetate solution to avoid decomposition of the product (method 19).

An attempt was made to prepare 2-(diethylamino)ethyl pentachlorophenyl carbonate from 2-(diethylamino)ethanol and pentachlorophenyl chloroformate. An excess of the amino alcohol was used as the acid acceptor. The only products isolated were bis[2-(diethylamino)ethyl] carbonate (as the dihydrochloride) and pentachlorophenol. A mechanism which explains the formation of these products

Table I. Pentachlorophenyl Carbonates

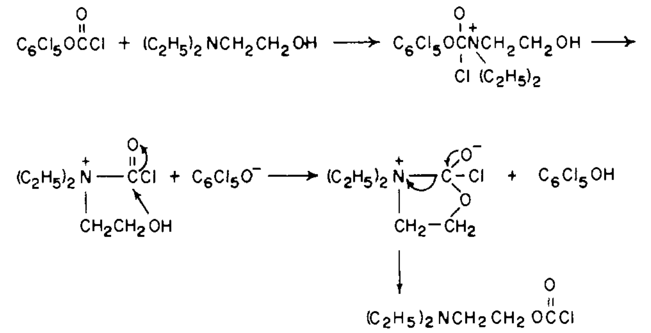


	R	Method	Yield, %	M.P., ° C. (B.P., ° C./mm. Hg)
1	$CH_3(CH_2)_3CH(C_2H_5)CH_2$	1	86	(218–219/1.4–1.6)
2	$CH_3(CH_2)_9{}^{a}$	2	47	39–40
3	$ClCH_2CH_2{}^{b}$	3	90	82–83
4	$BrCH_2CH_2$	4	24	91–92
5	CCl_3CH_2	4	46	110–111
6	$ClCH_2CH_2CH_2$	5	62	66–67
7	$ClCH_2CH(CH_3)$	2	29	64–65
8	$ClCH_2CH(Cl)CH_2$	4	16	75–77
9	$ClCH_2CH(CH_2Cl)$	6	43	122–123
10	$ClCH_2CH_2CH_2CH_2$	4	10	69–70
11	$ClCH{=}CHCH_2$	2	12	75–76
12	$CH{\equiv}CCH_2$	4	42	107–108
13	$HOCH_2CH_2$	7	23	141–142
14	$CH_3OCH_2CH_2$	2	48	73–74
15	2,4-$Cl_2C_6H_3OCH_2CH_2$	8	55	155–156
16	$CH_3CH_2SCH_2CH_2$	2	46	63–64
17	$CH_3CH_2OCOCH(CH_3)$	2	33	110–111
18	$CNCH_2CH_2$	2	21	116–118
19	$CH_3CH_2CH(NO_2)CH_2$	2	4	110–112
20	C_6H_5	5^{c}	72	108–109
21	4-ClC_6H_4	9	94	124–125
22	3,4,5-$Cl_3C_6H_2$	10	86	187–188

	Formula	Carbon, %		Hydrogen, %		Chlorine, %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
1	$C_{15}H_{17}Cl_5O_3$	42.6	42.6	4.05	4.15	41.9	41.9
2	$C_{17}H_{21}Cl_5O_3$	45.3	45.0	4.70	4.73	39.3	39.6
3	$C_9H_4Cl_6O_3$	29.0	28.9	1.08	1.25	57.1	57.0
4	$C_9H_4BrCl_5O_3$	25.9	26.2	0.97	1.22		
5	$C_9H_2Cl_8O_3$	28.5	24.3	0.45	0.86	64.2	64.3
6	$C_{10}H_6Cl_6O_3$	33.0	30.7	1.56	1.22	55.0	54.9
7	$C_{10}H_6Cl_6O_3$	31.2	30.9	1.56	1.62	55.0	55.1
8	$C_{10}H_5Cl_7O_3$	28.5	28.4	1.20	1.39	58.9	58.6
9	$C_{10}H_5Cl_7O_3$	38.5	28.5	1.20	1.39	58.9	58.8
10	$C_{11}H_8Cl_6O_3$	33.0	33.1	2.01	2.27	53.1	53.2
11	$C_{10}H_4Cl_6O_3$	31.2	31.4	1.05	1.30	55.3	55.4
12	$C_{10}H_3Cl_5O_3$	34.5	34.6	0.87	1.04	50.9	51.2
13	$C_9H_5Cl_5O_4$	30.5	30.7	1.42	1.59	50.0	49.8
14	$C_{10}H_7Cl_5O_4$	32.6	32.6	1.91	2.12	48.1	48.2
15	$C_{15}H_7Cl_7O_4$	36.1	36.1	1.41	1.30	49.7	49.5
16	$C_{11}H_9Cl_5O_3S^{d}$	33.2	33.1	2.28	2.51	44.5	44.6
17	$C_{12}H_9Cl_5O_5$	35.1	35.2	2.21	2.46	43.2	43.3
18	$C_{10}H_4Cl_5NO_3{}^{e}$	33.1	33.2	1.11	1.15	48.8	48.8
19	$C_{11}H_8Cl_5NO_5{}^{f}$	32.1	32.0	1.96	2.10		
20	$C_{13}H_5Cl_5O_3$	40.4	40.3	1.30	1.32	45.9	45.7
21	$C_{13}H_4Cl_6O_3$	37.1	37.0	0.96	1.10	50.5	50.6
22	$C_{13}H_2Cl_8O_3$	31.9	31.9	0.41	0.57	57.9	57.5

[a] Compounds 2, 7, and 11 were recrystallized from pentane; 3–5, 12, 14, 18, and 20–22 from methylcyclohexane; 6 from heptane; 8–10, 16, 17, and 19 from hexane; 13 from hexane-benzene, and 15 from toluene. [b] Prepared initially by R.H. Mills, Monsanto Co. [c] The reactants were phenyl chloroformate and pentachlorophenol. [d] Calcd. S, 8.05. Found: 8.10. [e] Calcd. N, 3.85, Found: 3.77. [f] Calcd. N, 3.40. Found: 3.30.

represents a type of acid chloride interchange and is shown below.



In this mechanism, interaction of the amino group of the alcohol with the chloroformate forms the expected addition product, which expels the bulky pentachlorophenate anion. The resulting intermediate undergoes cyclization and loses a hydrogen ion which combines with the pentachlorophenate anion to form pentachlorophenol. Ring opening of the cyclic intermediate yields 2-(diethylamino)ethyl chloroformate which then undergoes reaction with additional amino alcohol to form the bis-carbonate.

The cyclic carbonates were prepared by the addition of phosgene to a benzene solution of the catechol and pyridine. Attempts to prepare these compounds from the disodium salt of the catechol and phosgene, a procedure utilized for the preparation of analogous compounds (*6*), were unsuccessful. The dicarbonates of dihydric phenols were prepared directly by the addition of triethylamine to an ether solution of the phenol and chloroformate (1:2 molar ratio).

The infrared spectra of a number of representative compounds were examined and the adsorptions agreed with the values reported (*12*) for similar carbonates.

EXPERIMENTAL

Melting points, taken on a Fisher-Johns Melting Point Apparatus, and boiling points are corrected.

Chloroformates. Most of the chloroformates required were obtained commercially. *p*-Chlorophenyl (*13*) and pentachlorophenyl (*8*) chloroformate were prepared in a manner similar to that reported in the literature.

2,4,5-Trichlorophenyl Chloroformate. This chloroformate was prepared from 2,4,5-trichlorophenol and phosgene by a procedures employed for the preparation of similar chloroformates (*13*); m.p. 64-65° (from hexane); 62% yield.

Anal. Calcd. for $C_7H_2Cl_4O_2$: Cl, 54.6. Found: Cl, 54.5.

2-Benzyl-4-chlorophenyl Chloroformate. A solution of 212.0 grams (2.1 moles) of phosgene in 250 ml. of toluene was stirred at −50° for two to three hours while portions of a total of 481.3 grams (2 moles) of sodium 2-benzyl-4-chlorophenate suspended in 50 ml. of toluene were added. The mixture was stirred at room temperature for 16 hours, excess phosgene and most of the toluene were removed under reduced pressure, and the sodium chloride was removed by filtration. The remainder of the toluene was distilled from the filtrate and the residual oil was fractionated; b.p. 153-160° (0.75-1.35 mm. of Hg); 58% yield. This intermediate was characterized by conversion to compound 47, Table II.

Carbonates. METHOD 1. A mixture of the required phenol (0.2 mole) and 600 ml. of pyridine was stirred at 0-10° during the dropwise addition of the required alkyl chloroformate (0.3 mole). The suspension was stirred overnight at room temperature. Excess pyridine was removed at a pot temperature of 40-45° (15 mm. of Hg), the residue was treated with 500 ml. of 3*N* sodium hydroxide solution, and the mixture was extracted with ether. The extract was washed successively with sodium hydroxide solution and water and dried over magnesium sulfate. The solvent was removed and the residue was distilled through an 11 inch Vigreux column.

METHOD 2. A mixture of pentachlorophenyl chloroformate or 2,4,5-trichlorophenyl chloroformate, the required alcohol (0.05 mole of each), and 150 ml. of anhydrous ether was stirred at 0-5° during the dropwise addition over a 30 min. period of pyridine (0.05 mole) dissolved in 25 ml. of ether. The mixture was stirred at 25-35° for three hours and filtered to remove the insoluble by-products. The ether was removed from the filtrate under reduced pressure and the residue was purified by recrystallization after decolorization with activated carbon, when required.

METHOD 3. A solution of sodium pentachlorophenate (0.1 mole) in 190 ml. of water was stirred at 3° during the dropwise addition of 2-chloroethyl chloroformate (0.1 mole). At the end of the addition the pH was adjusted to 8 with 20% aqueous sodium hydroxide solution, if required, and the mixture was stirred for one hour while the temperature was allowed to rise to 20°. The crude product was collected, washed with water, dried, and recrystallized.

METHOD 4. A mixture of pentachlorophenyl chloroformate, the required alcohol (0.05 mole of each), 150 ml. of heptane, and 50 ml. of benzene was stirred at room temperature during the dropwise addition over a 30 min. period of triethylamine (0.05 mole) dissolved in 25 ml. of benzene. The mixture was stirred and refluxed for six hours, and the product was isolated as described in Method 2.

METHOD 5. A mixture of the required phenol, alkyl chloroformate (0.1 mole of each), and 175 ml. of toluene or ether was stirred at 30° during the dropwise addition over a 20 min. period of triethylamine (0.1 mole) dissolved in 25 ml. of toluene or ether. The mixture was stirred and refluxed for four to six hours, cooled, and filtered to remove the precipitated triethylamine hydrochloride. The solvent was removed from the filtrate and the residue was distilled in vacuo or recrystallized after decolorization with activated carbon, when required.

METHOD 6. This procedure was the same as Method 2 except that toluene was substituted for ether and the reaction mixture was stirred at 110° for three hours.

METHOD 7. This method was like Method 2 except that a tenfold excess of ethylene glycol was used in place of the alcohol. The excess was used in order to retard formation of the dicarbonate.

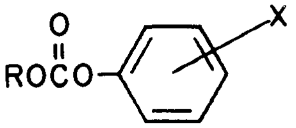
METHOD 8. A solution of pentachlorophenyl chloroformate and 2-(2,4-dichlorophenoxy)ethanol (0.025 mole of each) in 50 ml. of xylene was stirred at 140° for eight hours. The solvent was removed and the residue was recrystallized.

METHOD 9. Pentachlorophenol or 3,4-dichlorophenol and the required chloroformate was allowed to react as described in Method 5; ether was used as the solvent. Part of the product precipitated with the triethylamine hydrochloride and, after the filtration, it was separated by treatment with water.

METHOD 10. A solution of pentachlorophenol and triethylamine (0.025 mole of each) in 300 ml. of ether was stirred at 3° during the dropwise addition over a period of one hour of 2,4,5-trichlorophenyl chloroformate (0.025 mole) dissolved in 150 ml. of ether. The suspension was stirred for three hours at room temperature and allowed to stand overnight. The insoluble material was removed by filtration and washed with ether. Part of the crude product was obtained by removing the ether from the filtrate. The major portion of the product was obtained by treating the separated solid material with water and filtering.

METHOD 11. The reaction and work-up procedure were the same as in Method 1 except that the excess pyridine was removed at mild temperatures (25-30°) under lower pressure (2-3 mm. of Hg) to retard quaternary salt formation between pyridine and the 2-chloroethyl group.

Table II. Halophenyl Carbonates



	R	X	Method	Yield, %	M.P., ° C. (B.P., ° C./mm. Hg)
23	$ClCH_2CH_2$	2,4-Br_2	5	93	(145–150/0.4)
24	4-ClC_6H_4[a]	3,4-Cl_2	9	92	144–145
25	CH_3CH_2	2,4,5-Cl_3	1	85	58–59[b] (132–133/3.4)
26	$CH_3(CH_2)_3$	2,4,5-Cl_3	1	94	(146–147/2.5)
27	$CH_3(CH_2)_5$	2,4,5-Cl_3	1	93	(160–161/1.5)
28	$CH_3(CH_2)_3CH(C_2H_5)CH_2$	2,4,5-Cl_3	1	84	(195–196/5.0)
29	$CH_2=CHCH_2$	2,4,5-Cl_3	1	50	61–62[c] (154–155/0.6)
30	$ClCH_2CH_2$	2,4,5-Cl_3	11	89	64–65 (178–179/0.6)
31	$C_6H_5OCH_2CH_2$	2,4,5-Cl_3	2	95	55–56
32	$(CH_3)_2C(NO_2)CH_2$	2,4,5-Cl_3	2	64	123–125
33	$ClCH_2CH_2$	2,4,6-Cl_3	5	52	(137–139/0.9–1.0)
34	$ClCH_2CH_2$	2,3,4,6-Cl_4	5	100	54–55
35	$ClCH_2CH_2$	2,3,4,5,6-Br_5	5	78	130–131
36	$ClCH_2CH_2$	2,3,4,5-Cl_4-6-OCH_3	5	67	90–92
37	$ClCH_2CH_2$	2,3,5,6-Cl_4-4-OCH_3	12	96	96–97
38	$ClCH_2CH_2$	2,3,4,5-Cl_4-6-OH	13	31	105–106
39	CH_3CH_2	2-$C_6H_5CH_2$-4-Cl	1	96	43–44 (160–162/1.0)
40	$CH_3CH_2CH_2$	2-$C_6H_5CH_2$-4-Cl	1	92	(166–167/1.2)
41	$CH_3(CH_2)_3$	2-$C_6H_5CH_2$-4-Cl	1	92	(175–176/1.1–1.2)
42	$CH_3CH(CH_3)CH_2$	2-$C_6H_5CH_2$-4-Cl	1	92	(172–174/1.3)
43	$CH_3(CH_2)_5$	2-$C_6H_5CH_2$-4-Cl	1	94	(196–197/1.0)
44	$CH_2=CHCH_2$	2-$C_6H_5CH_2$-4-Cl	1	72	(144–148/0.3)
45	$ClCH_2CH_2$	2-$C_6H_5CH_2$-4-Cl	11	81	(187–189/0.8)
46	$C_6H_5CH_2$	2-$C_6H_5CH_2$-4-Cl	14	78	(198–199/0.3)
47	2-$C_6H_5CH_2$-4-ClC_6H_3	2-$C_6H_5CH_2$-4-Cl	2	75	132–133

		Carbon, %		Hydrogen, %		Chlorine, %	
	Formula	Calcd.	Found	Calcd.	Found	Calcd.	Found
23	$C_9H_7Br_2ClO_3$	30.2	30.2	1.97	2.21	9.89	10.2
24	$C_{13}H_7Cl_3O_3$	49.2	49.2	2.22	2.31	33.5	33.6
25	$C_9H_7Cl_3O_3$	40.1	40.2	2.61	2.72	39.5	39.6
26	$C_{11}H_{11}Cl_3O_3$	44.4	44.6	3.72	3.74		
27	$C_{13}H_{15}Cl_3O_3$	47.9	48.0	4.64	4.76		
28	$C_{15}H_{19}Cl_3O_3$	50.9	51.0	5.41	5.67		
29	$C_{10}H_7Cl_3O_3$	42.7	42.8	2.50	2.60	37.8	37.7
30	$C_9H_6Cl_4O_3$	35.6	35.7	1.98	2.24	46.6	46.2
31	$C_{15}H_{11}Cl_3O_4$	49.8	49.9	3.07	3.26	29.4	29.3
32	$C_{11}H_{10}Cl_3NO_5$[d]	38.6	38.7	2.94	3.02	31.0	31.0
33	$C_9H_6Cl_4O_3$	35.6	35.5	1.99	2.23	46.7	46.5
34	$C_9H_5Cl_5O_3$	31.9	31.9	1.49	1.60	52.4	52.6
35	$C_9H_4Br_5ClO_3$	18.2	18.2	0.68	0.77		
36	$C_{10}H_7Cl_5O_4$	32.6	32.3	1.91	1.90	48.1	48.0
37	$C_{10}H_7Cl_5O_4$	32.6	32.3	1.91	2.00	48.1	48.0
38	$C_9H_5Cl_5O_4$	30.5	30.5	1.42	1.52	50.0	50.0
39	$C_{16}H_{15}ClO_3$	66.1	66.1	5.20	5.34	12.2	12.3
40	$C_{17}H_{17}ClO_3$	67.0	66.9	5.62	5.64	11.6	11.6
41	$C_{18}H_{19}ClO_3$	67.8	67.8	6.00	6.17	11.1	11.2
42	$C_{18}H_{19}ClO_3$	67.8	67.8	6.00	6.00	11.1	11.2
43	$C_{20}H_{23}ClO_3$	69.3	69.4	6.68	6.81	10.2	10.2
44	$C_{17}H_{15}ClO_3$	67.4	67.4	4.99	5.03	11.8	11.9
45	$C_{16}H_{14}Cl_2O_3$	59.1	59.1	4.34	4.31	21.8	21.9
46	$C_{21}H_{17}ClO_3$	71.5	71.1	4.85	4.89	10.0	10.1
47	$C_{27}H_{20}Cl_2O_3$	70.0	69.8	4.35	4.48	15.3	14.9

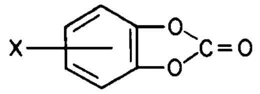
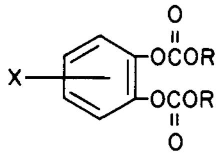
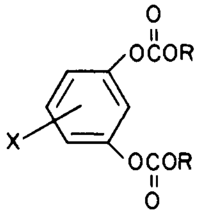
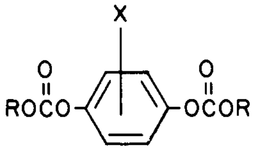
[a] Compound 24 was recrystallized from toluene; 31 and 32 from methylcyclohexane-toluene; 34, 36, and 37 from hexane; 35 from methylcyclohexane; 38 from acetonitrile and 47 from ethanol. [b] Lit. (*11*) m.p. 56–57°. [c] Lit. (*11*) m.p. 62.5°. [d] Calcd. N, 4.09, Found: 4.40.

METHOD 12. This procedure was like Method 5 except that pyridine was substituted for triethylamine and the chloroformate solution was added at 1–3°; ether was used as the solvent.

METHOD 13. A mixture of tetrachlorocatechol (0.05 mole) and 250 ml. of ether was stirred at 25° during the dropwise addition of triethylamine (0.05 mole) dissolved in 15 ml. of ether. A solution of 2-chloroethyl chloroformate (0.05 mole) in 25 ml. of ether was then added dropwise over a 30 min. period while the mixture was stirred at 5°. The mixture was stirred and refluxed for four hours and the insoluble by-products were removed by filtration. The solvent was removed from the filtrate and the residue was recrystallized.

METHOD 14. A mixture of benzyl chloroformate, 2-benzyl-

Table III. Carbonates of Dihydric Phenols

	R	X	Method	Yield, %	M.P., ° C.
					
48[a]		$4,5\text{-}Cl_2$[b]	15	75	76-77
49		$3,4,5,6\text{-}Cl_4$	15	75	172-173
					
50	CH_3	$3,4,5,6\text{-}Cl_4$	16	96	121-122
51	CH_3CH_2	$3,4,5,6\text{-}Cl_4$	16	99	90-91
52	$CH_3(CH_2)_3$	$3,4,5,6\text{-}Cl_4$	16	80	19-20
53	$ClCH_2CH_2$	$3,4,5,6\text{-}Cl_4$	16	55	69-71
54	$ClCH_2CH_2$	$3,4,5,6\text{-}Br_4$	16	19	118-119
					
55	$ClCH_2CH_2$	$4,6\text{-}Cl_2$	16	72	87-88
56	C_6H_5	4-Cl	16	67	120-121
					
57	$ClCH_2CH_2$	$2,3,5,6\text{-}Cl_4$	16	78	125-127

		Carbon, %		Hydrogen, %		Chlorine, %	
	Formula	Calcd.	Found	Calcd.	Found	Calcd.	Found
48	$C_7H_2Cl_2O_3$					34.6	34.9
49	$C_7Cl_4O_3$	30.7	30.7			51.8	52.1
50	$C_{10}H_6Cl_4O_6$	33.0	33.2	1.66	1.91	39.0	39.3
51	$C_{12}H_{10}Cl_4O_6$	36.8	36.4	2.57	2.60	36.2	36.2
52	$C_{16}H_{18}Cl_4O_6$	42.9	42.9	4.05	3.97	31.7	31.8
53	$C_{12}H_8Cl_6O_6$	31.3	31.0	1.75	1.90	46.2	46.1
54	$C_{12}H_8Br_4Cl_2O_6$	22.6	22.8	1.26	1.40	11.1	11.2
55	$C_{12}H_{10}Cl_4O_6$	36.8	36.5	2.57	2.81	36.2	36.2
56	$C_{20}H_{13}ClO_6$	62.4	62.4	3.46	3.55	9.22	9.30
57	$C_{12}H_8Cl_6O_6$	31.3	31.1	1.75	1.83	46.2	46.4

[a] Compounds 48-51 and 54-57 were recrystallized from methyl cyclohexane; 52 from pentane and 53 from methylcyclohexane-toluene.

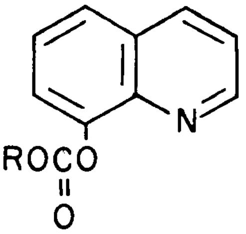
[b] Prepared by Ignatius Schumacher, Monsanto Co.

4-chlorophenol (0.2 mole of each), sodium carbonate (0.1 mole), and 400 ml. of benzene was stirred at 40-50° during the dropwise addition of 50 ml. of 4*N* sodium hydroxide solution. The mixture was then stirred at 50° for 16 hours. The benzene layer was separated, washed with 1.5*N* sodium hydroxide solution, and dried over sodium sulfate. The solvent was removed under reduced pressure and the residue was distilled in vacuo through an 11 inch Vigreux column.

METHOD 15. A mixture of the required catechol (0.05 mole), pyridine (0.1 mole), and 400 ml. of benzene was stirred at 5-10° during the subsurface introduction over a 10 min. period of phosgene (0.5 mole). The mixture was stirred at room temperature for 1.5 hours and the insoluble by-products were removed by filtration. The solvent was removed from the filtrate and the residue was recrystallized.

METHOD 16. A mixture of the required dihydric phenol (0.1 mole), the required chloroformate (0.2 mole) and 350 ml. of ether was stirred at 10-15° during the dropwise addition of triethylamine (0.2 mole) dissolved in 25 ml. of ether. The mixture was stirred and refluxed for three hours, cooled to room temperature, and filtered to remove the insoluble material. The crude product was obtained by removal of the solvent from the filtrate and, in some cases, by also treating the solids obtained above with water. The products were purified by recrystallization after decolorization with activated carbon, when required.

Table IV. 8-Quinolyl Carbonates



	R	Method	Yield, %	M.P., ° C. (B.P., ° C./mm. Hg)
58	CH_3	17	72	60-62 (160-162/2.0)
59	CH_3CH_2[a]	1	79	110-111 (156-157/1.5)
60	$CH_3CH_2CH_2$	1	93	57-58 (160-161/1.4)
61	$CH_3(CH_2)_3$[b]	1	94	54-55 (168-169/1.1)
62	$CH_3CH(CH_3)CH_2$	1	96	(163-164/1.1)
63	$CH_3(CH_2)_5$	1	92	(183-184/1.4)
64	$CH_3(CH_2)_3CH(C_2H_5)CH_2$	1	86	(217-218/3.3)
65	$CH_2{=}CHCH_2$	1	66	54-55 (160-170/0.65)
66	$ClCH_2CH_2$	11	33	68-69
67	C_6H_5	18	68	82-83
68	$4\text{-}ClC_6H_4$	19	90	118-119

		Carbon, %		Hydrogen, %		Nitrogen, %	
	Formula	Calcd.	Found	Calcd.	Found	Calcd.	Found
58	$C_{11}H_9NO_3$	65.0	64.8	4.47	4.40	6.89	7.00
59	$C_{12}H_{11}NO_3$	66.3	66.5	5.10	5.11	6.44	6.50
60	$C_{13}H_{13}NO_3$	67.5	67.6	5.66	5.75	6.05	6.23
61	$C_{14}H_{15}NO_3$	68.5	68.4	6.16	6.46	5.71	5.75
62	$C_{14}H_{15}NO_3$	68.5	68.3	6.16	6.20	5.71	5.80
63	$C_{16}H_{19}NO_3$	70.3	70.2	7.00	6.88	5.12	5.43
64	$C_{18}H_{23}NO_3$	71.7	71.5	7.69	7.74	4.64	4.80
65	$C_{13}H_{11}NO_3$	68.1	68.4	4.83	5.06	6.11	6.28
66	$C_{12}H_{10}ClNO_3$[c]	57.3	57.2	4.00	4.20	5.56	5.38
67	$C_{16}H_{11}NO_3$	72.4	72.6	4.18	4.40	5.28	5.10
68	$C_{16}H_{10}ClNO_3$[d]	64.1	64.1	3.33	3.43	4.67	4.77

[a] Lit. m.p. 110-111° (*9*). [b] Compounds 61 and 66 were recrystallized from methylcyclohexane; 67 from methylcyclohexane-toluene and 68 from hexane. [c] Calcd. Cl, 14.1. Found: 14.1. [d] Calcd. Cl, 11.8. Found: 11.9

Method 17. A solution of 8-quinolinol (0.4 mole) and pyridine (0.44 mole) in 300 ml. of ether was added dropwise over a period of 1.5 hours to a stirred, ice-cold solution of methyl chloroformate (0.44 mole) in 500 ml. of ether. The mixture was stirred at room temperature for six hours and filtered. The ether was removed from the filtrate and the oily residue was distilled under reduced pressure.

Method 18. This procedure was the same as Method 17 except that equimolar quantities of reactants were used and the product was purified by recrystallization.

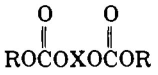
Method 19. Pyridine (600 ml.) containing 8-quinolinol (0.2 mole) was treated with the required aryl chloroformate (0.2 mole) at room temperature by dropwise addition. The reaction was slightly exothermic. The mixture was stirred at 40° for 16 hours and excess pyridine was removed under reduced pressure with mild heating. The remaining slurry was hydrolyzed with excess 1*M* sodium acetate. Part of the crude product was obtained by filtration, and the remainder by extraction with ether. The combined ether extracts were dried over magnesium sulfate. The solvent was removed and the residue was combined with the filtration product for recrystallization.

Method 20. This procedure was the same as Method 1 except that 2 moles of substituted phenol were used with each mole of bis-chloroformate (compounds 69-73, 75-77) and 2 moles of chloroformate were used with each mole of bis-phenol (compounds 78-83). The products were practically insoluble in ether and were readily isolated by filtration. The filtered materials were washed successively with ether, cold 3*N* sodium hydroxide solution, and water and then recrystallized, when required.

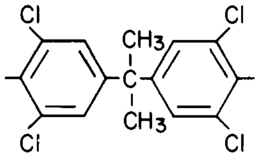
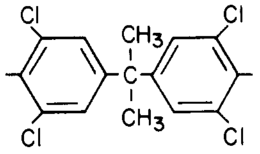
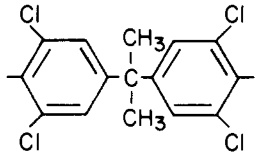
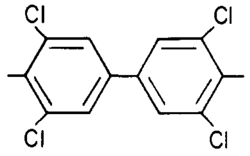
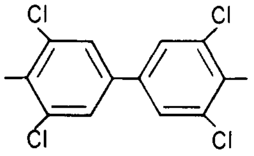
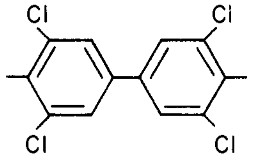
Method 21. A mixture of pentachlorophenyl chloroformate (0.05 mole), the diol (0.025 mole), and 400 ml. of ether was stirred at 2-3° during the dropwise addition over a period of 30 min. of pyridine (0.05 mole) dissolved in 25 ml. of ether. The mixture was stirred at room temperature for three hours, the insoluble by-products were removed by filtration, and the solvent was removed from the filtrate. The residue was purified by recrystallization.

Bis[2-(diethylamino)ethyl] Carbonate from Pentachlorophenyl Chloroformate and 2-(Diethylamine)ethanol. An attempt was made to prepare 2-(diethylamino)ethyl pentachlorophenyl carbonate by a modification of Method 2 in

Table V. Dicarbonates



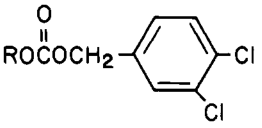
$RO\overset{O}{\overset{\|}{C}}OXO\overset{O}{\overset{\|}{C}}OR$

	R	X	Method	Yield, %	M.P., ° C.
69	8-Quinolyl[a]	CH_2CH_2	20	82	169-170
70	8-Quinolyl	$CH_2CH_2OCH_2CH_2$	20	62	111-112
71	C_6Cl_5	CH_2CH_2	20	42	202-203
72	C_6Cl_5	$CH_2CH_2OCH_2CH_2$	20	62	158-159
73	C_6Cl_5	$CH_2CH_2OCH_2CH_2OCH_2CH_2$	20	80	138-139
74	C_6Cl_5	$(CH_2)_{10}$	21	18	106-107
75	2,4,5-$Cl_3C_6H_2$	$CH_2CH_2OCH_2CH_2$	20	33	119-120
76	2-Cl-4-$NO_2C_6H_3$	CH_2CH_2	20	55	149-150
77	2-Cl-4-$NO_2C_6H_3$	$CH_2CH_2OCH_2CH_2$	20	59	83-84
78	CH_3CH_2		20	94	154-155
79	$CH_3(CH_2)_3$		20	88	93-94
80	$CH_3(CH_2)_5$[b]		20	64	81-82
81	CH_3CH_2		20	89	223-224
82	$CH_3(CH_2)_3$		20	81	115-116
83	$CH_3(CH_2)_5$		20	84	104-105

	Formula	Carbon, %		Hydrogen, %		Chlorine, %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
69	$C_{22}H_{16}N_2O_6$[c]	65.3	65.4	3.98	4.11		
70	$C_{24}H_{20}N_2O_7$[d]	64.3	64.2	4.49	4.46		
71	$C_{16}H_4Cl_{10}O_6$	29.7	29.9			54.8	54.4
72	$C_{18}H_8Cl_{10}O_7$	31.3	31.3	1.16	1.40	51.3	50.8
73	$C_{20}H_{12}Cl_{10}O_8$					48.2	47.8
74	$C_{24}H_{20}Cl_{10}O_6$	38.0	38.2	2.66	2.60	46.7	46.9
75	$C_{18}H_{12}Cl_6O_7$	39.1	39.5	2.18	2.37	38.5	38.0
76	$C_{16}H_{10}Cl_2N_2O_{10}$[e]	41.7	41.6	2.18	2.30	15.4	15.3
77	$C_{18}H_{14}Cl_2N_2O_{11}$[f]	42.8	42.6	2.79	3.07	14.0	14.0
78	$C_{21}H_{20}Cl_4O_6$	49.4	49.4	3.95	3.89	27.8	27.6
79	$C_{25}H_{28}Cl_4O_6$	53.0	53.0	4.98	5.04	25.0	25.0
80	$C_{29}H_{36}Cl_4O_6$	55.9	55.7	5.83	5.73	22.8	22.7
81	$C_{18}H_{14}Cl_4O_6$	46.2	46.2	3.01	3.07	30.3	30.2
82	$C_{22}H_{22}Cl_4O_6$	50.4	50.2	4.23	4.35	27.1	27.0
83	$C_{26}H_{30}Cl_4O_6$	53.8	53.8	5.21	5.04	24.4	24.3

[a] Compounds 69, 70, and 72-76 were recrystallized from toluene. [b] Prepared initially by H.C. Godt, Jr., Monsanto Co. [c] Calcd. N, 6.92. Found: 6.95. [d] Calcd. N, 6.24. Found: 6.26. [e] Calcd. N, 6.07. Found 6.09. [f] Calcd. N, 5.54. Found: 5.54.

Table VI. 3,4-Dichlorobenzyl Carbonates



	R	Method	Yield, %	B.P., ° C./mm. Hg
84	CH_3CH_2	1	88	110-111/0.2
85	$CH_3(CH_2)_3$	1	92	132-133/0.5
86	$CH_3(CH_2)_5$	1	85	146-147/0.45
87	$ClCH_2CH_2$	11	88	147-149/0.2

		Carbon, %		Hydrogen, %		Chlorine, %	
	Formula	Calcd.	Found	Calcd.	Found	Calcd.	Found
84	$C_{10}H_{10}Cl_2O_3$	48.2	48.4	4.04	4.26	28.5	28.5
85	$C_{12}H_{14}Cl_2O_3$	52.0	51.9	5.09	5.05	25.6	25.6
86	$C_{14}H_{18}Cl_2O_3$	55.1	55.1	5.94	5.99	23.2	23.3
87	$C_{10}H_9Cl_3O_3$	42.3	42.2	3.19	3.27	37.5	37.4

which an extra molar equivalent of 2-(diethylamino)ethanol was used as the hydrogen chloride acceptor instead of pyridine. The desired carbonate was not isolated. Instead, the biscarbonate, an oil (*4*), was obtained and it was precipitated as the dihydrochloride from ether solution; m.p. 218-219° (from absolute ethanol); 52% yield.

Anal. Calcd. for $C_{13}H_{30}Cl_2N_2O_3$: C, 46.8; H, 9.07; Cl, 21.3; N, 8.41. Found: C, 46.7; H, 9.10; Cl, 21.5; N, 8.11.

Pentachlorophenol was obtained as a by-product (36% yield) from the ether solution after precipitation and collection of dihydrochloride.

O-(2-Chloroethyl) S-Pentachlorophenyl Thiocarbonate. This compound was prepared from pentachlorothiophenol and 2-chloroethyl chloroformate by Method 5; m.p. 83-84° (from heptane); 62% yield.

Anal. Calcd. for $C_9H_4Cl_6O_2S$: C, 27.8; H, 1.04; Cl, 54.7; S, 8.24. Found: C, 27.9; H, 1.17; Cl, 54.8; S, 8.20.

S-Phenyl O-(8-Quinolyl) Thiocarbonate. Reaction of 8-quinolinol and phenyl chlorothiolformate according to Method 1 yielded this product; m.p. 123-124° (from heptane); 72% yield.

Anal. Calcd. for $C_{16}H_{11}NO_2S$: C, 68.3; H, 3.94; N, 4.97; S, 11.4 Found: C, 68.1; H, 3.97; N, 4.95; S, 11.5.

Treatment of Pentachlorophenyl Chloroformate with Triethylamine. A solution of 13.2 grams (0.04 mole) of pentachlorophenyl chloroformate in 150 ml. of commercial anhydrous ether was stirred at 5° during the dropwise addition over a period of 10 min. of 1.0 gram (0.01 mole) of triethylamine dissolved in 25 ml. of ether. Insoluble material formed during the addition. The suspension was stirred at 5° for one hour, refluxed for two hours, and cooled. The product was collected and the filtrate was retained; weight, 7.2 grams; m.p. 275-277° (prior shrinking).

The analysis was calculated for an equimolar mixture of bis(pentachlorophenyl) carbonate and $(CH_3CH_2)_3\overset{+}{N}COCl$ Cl^-, $C_{20}H_{15}Cl_4NO_4$: C, 31.6; H, 1.99; Cl, 56.1; N, 1.85. Found: C, 31.8; H, 2.09; Cl, 56.1; N, 1.75.

The infrared spectrum (Nujol mull) corresponded to the spectrum of an authentic sample (*1*) of bis(pentachlorophenyl) carbonate except for medium to weak bands at 668, 1040, 2500, and 2575 cm.$^{-1}$ not present in the spectrum of the carbonate.

Treatment of a portion of the above product with water yielded bis(pentachlorophenyl) carbonate; m.p. 277-278°, lit. m.p. 265-268° (*2*). The infrared spectrum was identical with that of an authentic sample and a mixed melting point was not depressed.

Anal. Calcd. for $C_{13}Cl_{10}O_3$: Cl, 63.5. Found: Cl, 63.2.

The ether was removed in vacuo from the filtrate retained above to yield 6.7 grams of unreacted pentachlorophenyl chloroformate; m.p. 56-58°.

INFRARED SPECTRA

The infrared spectra (Nujol mull) of bis(pentachlorophenyl) carbonate and compounds 16, 20, 21, 22, 25, 29, 51, 55, 57, 60, 67, 69, 71, 74, 76, 79, and 81 and thin film spectra of compounds 33 and 86 and the spectra of compounds 3, 6, 7, 9, 10, and 58 in carbon disulfide solution were recorded on a Beckman IR-5 Spectrophotometer. The carbonyl absorptions occurred between 1745 and 1800 cm.$^{-1}$ depending on the substituents. The individual ranges corresponding to diaryl, dialkyl or aryl alkyl carbonates agreed with published values for related carbonates (*12*).

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