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Organosilicon Carbonates and Chlorocarbonates

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A systematic account is given for the first time of the methods of synthesis, properties, and practical applications of silicon-containing derivatives of carbonic acid—carbonates and chlorocarbonates (chloroformates). Together with monomeric compounds, oligomeric and polymeric products are discussed as well as other compositions from which new organosilicon articles with valuable practical properties, for example with a highly effective gas-separating capacity, have been made.
The bibliography includes 426 references.

CONTENTS

I. Introduction 1167
II. Compounds with the carbonate group at the silicon atom 1167
III. Organosilicon chlorocarbonates and carbonates with carbofunctional groups 1170
IV. Silicon-containing polycarbonates 1175
V. Practical applications of silicon-containing polycarbonates and related compounds 1179

I. INTRODUCTION

New organic and organosilicon polymeric materials and intermediates in their synthesis are now attracting an increased amount of attention [1-12]. This review is part of a series of previously published reviews dealing with carbonic acid derivatives: organosilicon isocyanates [13], ureas [14], and urethanes [15].

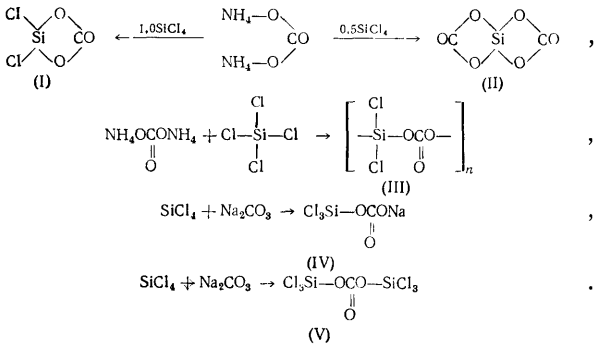
The chemistry of organic chlorocarbonates and carbonates has frequently been the subject of special and general reviews [16-21], but they were all published before studies on the synthesis of the corresponding silicon-containing derivatives were made and therefore naturally do not describe them or anticipate the possibility of their formation. Furthermore, in the last published review [22], the already available extensive data on this problem were not described. A fairly considerable amount of attention has been devoted to silicon-containing carbonic and chlorocarbonic acid esters in a number of studies [23-32], but the latter were incomplete, since they were devoted to specific problems. Carbonates are esters of carbonic acid which does not exist in a free state. Chloroformates may be regarded as esters of chloroformic or more correctly chlorocarbonic acid, because from the chemical point of view the transition from carbonic to its acid chloride is more apt than the transition from formic acid to chloroformic acid.

Depending on the relative positions of the ester $-OC(O)O-$ and silyl groups, silicon-containing carbonates (silyl carbonates) can be divided into two independent classes—compounds in which the above groups are linked directly (*O*-silyl carbonates) and organosilicon carbonates with carbofunctional substituents in which these fragments are separated by a carbon or similar bridge (*C*-silyl carbonates).

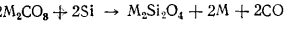
II. COMPOUNDS WITH THE CARBONATE GROUP AT THE SILICON ATOM

1. Methods of Synthesis

When $SiCl_4$ reacts with ammonium and alkali metal carbonates, the products are trichlorosilanol and chlorosiloxanes and not *O*-silyl carbonates [33], for example, compounds (I)-(V):



Nor were silyl esters of carbonic acid isolated in the interaction of inorganic carbonates M_2CO_3 (M = Li, Na, K, Rb, or Cs) with reactive finely divided silicon [34], since the process proceeded via the following mechanism:



and was accompanied by oxidation-reduction side reactions:

$$2CO \rightarrow CO_2 + C \quad ,$$
$$2M + CO \rightarrow M_2O + C \quad ,$$
$$Si + 2CO \rightarrow SiO_2 + 2C \quad .$$

The formation of $(Me_3SiO)_2CO$ as a result of an electrochemical reaction was observed by Butts and Rainey [35] by chromatographic and mass-spectrometric and analytical methods. However, the product was not isolated in a pure state.

At the end of 1971, Yamamoto and Tarbell [36] were the first to synthesise mixed alkyl trimethylsilyl carbonates [36]:

$$RONa \xrightarrow{CO_2} ROC(O)ONa \xrightarrow{Me_3SiCl} \underset{(VI)}{ROC(O)OSiMe_3} \quad ;$$

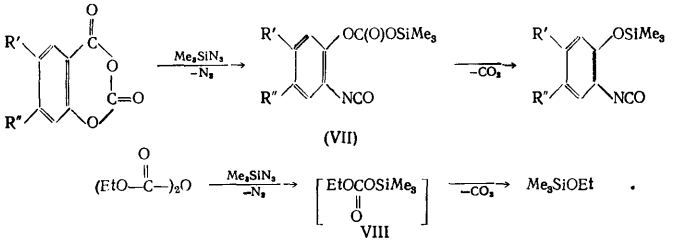
R = Et, iso-Pr, n-Bu, t-Bu, or iso-Pr_2CH.

Thio-analogues of the carbonates (VI) as well as the corresponding derivatives of other Group IVB elements, for example germanium, tin, and lead, are formed when alkyl thiocarbonates of alkali metals are acted upon by R'_3MX: [36,37]

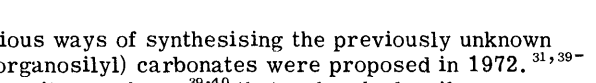
$$ROC(O)SM' + R'_3M{-}X \rightarrow ROC(O)SMR'_3 + M'X \quad ;$$

R = Et or t-Bu; M = Si, Ge, Sn, or Pb; M′ = K or Na; R′ = alkyl.

The asymmetric carbonates (VII) and (VIII) are unstable intermediates in the reaction of Me_3SiN_3 with carboxylic acid anhydrides [38]:

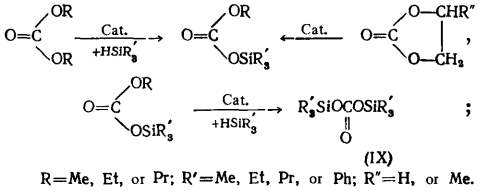


(VII)



VIII

Various ways of synthesising the previously unknown bis(triorganosilyl) carbonates were proposed in 1972. [31,39-42]. Thus it was shown [39,40] that, when hydrosilanes are made to react with dialkyl or alkylene carbonates in the presence of the Ni/Et_2S (or $NiCl_2$/$Me_3SiSiMe_3$) catalyst [43], stepwise displacement of the organic groups by triorganosilyl groups is observed, for example:



(IX)

R=Me, Et, or Pr; R′=Me, Et, Pr, or Ph; R″=H, or Me.

Compounds of type (IX) have been synthesised [31,41,42] by combining reactions involving treatment with phosgene, carboxylation, and protection by silyl groups:

$$R_3SiOH + COCl_2 \xrightarrow[-HCl]{Et_3N} \underset{(IX)}{R_3SiOC(O)OSiR_3} \leftarrow R_3SiONa + COCl_2 \quad ,$$

$$R_3SiONa \xrightarrow{CO_2} R_3SiOCONa \xrightarrow[-NaCl]{R_3SiCl} R_3SiOC(O)OSiR_3 \quad .$$

The last reaction served as the basis of the synthesis of *O*-silyl carbonates with different organosilyl groups [44]:

$$Et_3SiOH \xrightarrow[20°C]{NaH/THF} Et_3SiONa \xrightarrow[2.\ Me_3SiCl]{1.\ CO_2} \underset{(X)}{Et_3SiOCOSiMe_3} \quad .$$

A mixed anhydride of carbonic acid and triorganosilylcarbonic acid (XI) was obtained in the same investigation by treating $Et_3SiOC(O)ONa$ with phosgene:

$$Et_3SiOC(O)ONa + COCl_2 \rightarrow \underset{(XI)}{Et_3SiOCOCOSiEt_3} \quad .$$

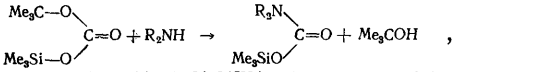
2. Physical Properties

The organosilicon carbonates $R_3SiOC(O)OR'$, $R_3SiOC(O)OSiR_3$, and $R_3SiOC(O)OSiR''_3$ (where R, R′, and R″ are alkyl groups) are colourless, transparent liquids or low-melting crystalline substances which can be vacuum-distilled without decomposition. Exceptions are $(Ph_3SiO)_2CO$, which melts at 160°C, $Me_3SiOC(O)OBu$-n, which decomposes with evolution of CO_2, and n-$BuOSiMe_3$, which decomposes even at room temperature [31,36,39-42,44]. The infrared spectra of the carbonates $R_3SiOC(O)OR'$ have ν(CO) bands in the ranges 1755–1760 and 1720–1730 cm^{-1}. The bands in the spectra of the compounds $R_2SiOC(O)OSiR_3$ are somewhat closer together and are located at 1705 to 1707 and 1740 cm^{-1}. The $(Ph_3SiO)_2CO$ spectrum has only a singlet at 1765 cm^{-1}. The calculated and observed molecular refractions are similar [39].

The ^1H NMR and mass spectra of silyl carbonates have been described [31,36,39,41,44].

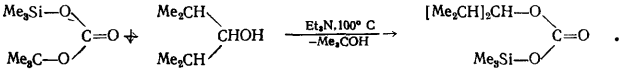
4. Chemical Properties

It has been shown [36] that, on treatment with primary and secondary amines, the carbonate $Me_3SiOC(O)OCMe$ is converted into the corresponding silyl carbamate esters†:



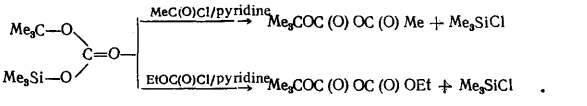
R_2=$(CH_2)_4$; $(CH_2)_5$; $(CH_2)_2O(CH_2)_2$; Ph and H; or Ph and Me.

while on reaction with a high-boiling alcohol it is transesterified:



This is evidence for a greater lability of the CO–C bond compared with SiO–C.

On the other hand, treatment with MeC(O)Cl and EtOC(O)Cl results in the cleavage of the Si–O bond:



Pyrolysis of the *O*-silyl carbonates (VI) and (IX) leads to alkoxysilanes and disiloxanes respectively [44]:

$$(VI) \xrightarrow{t_1} R_3SiOR' + CO_2 \quad ,$$
$$(IX) \xrightarrow{t_2>t_1} R_3SiOSiR_3 + CO_2 \quad .$$

† Phosphorus-containing carbonates behave similarly: the C–(O)OEt bond is cleaved by ammonia in preference to the C–(O)OP bond [45]:

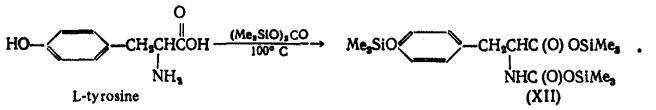
$$P(OCOEt)_3 + NH_3 \rightarrow P(OCNH_2)_3 + EtOH \quad .$$

Hydrolysis of the carbonates (IX) in a neutral medium takes place at a moderate rate with formation of R_3SiOH and CO_2. In the presence of inorganic acids, the process is sharply accelerated [31,39,41]:

$$(R_3SiO)_2CO + H_2O \xrightarrow[pH<7]{Me_2CO} R_3SiOH + CO_2 \quad .$$

The Grignard reaction with silyl carbonates proceeds via exactly the same mechanism as in the case of organic carbonates [46].

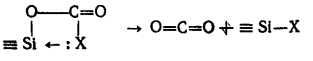
Bis(trimethylsilyl) carbonate behaves as a siloxycarbonylating and silylating agent on interaction with aminoacids [44]. For example, the reaction with L-tyrosine gave the tris(trimethylsiloxy)-derivative (XII):



L-tyrosine (XII)

4. β-Elimination Reactions

The products of the reaction of R_3SiH with dialkyl or alkylene carbonates contain alkoxysilanes and disiloxanes, which are apparently formed as a result of the β-decomposition of the intermediate and final organosilicon carbonates. The decomposition of the molecules is the final result of the electron redistribution in the system of σ bonds in the structural fragment $\equiv Si-O-C(O)-X$ (where X = OR or $OSiR_3$) as a consequence of the intramolecular coordination O: $\rightarrow Si\equiv$ in the four-membered transition complex:



$\rightarrow O=C=O + \equiv Si-X$.

In this respect organosilicon carbonates show similarities with stannyl carbonates [47-50]:

$$Bu_3Sn-OC(O)-OMe \xrightarrow{60-80° C} Bu_3Sn-OMe + O=C=O \quad ,$$
$$R_3Sn-OC(O)-OSnR_3 \xrightarrow{\sim 90° C} R_3SnOSnR_3 + O=C=O \quad ,$$

and plumbyl carbonates [48]:

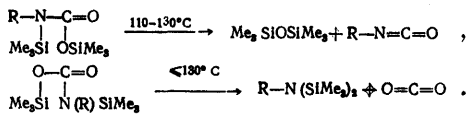
$$Ph_3Pb-OC(O)-OMe \xrightarrow{<110° C} Ph_3PbOMe + O=C=O.$$

The available data already permit the conclusion that the thermal stability of the compounds $R_3EOC(O)OR'$ and $(R_3EO)_2CO$ diminishes in series of similar compounds in the following sequence: C > Si > Sn > Pb. On the other hand, as for the compounds $\equiv Si-N(R)-C(O)-X$ (X = Cl, OR, or $OSiR_3$), [51] the thermal and chemical stability of the $R_3E-OC(O)-X$ (E = C, Si, Sn, or Pb) groups falls sharply with increasing electronegativity of X. A striking example of this is provided by the compound $Me_3C-OC(O)Cl$, which does not exist at room temperature [52-54], and by its silicon [28,31,55,56] and tin analogues, which are undoubtedly formed in the course of the following chemical reactions:

$$R_3SiCH_2CH_2OC(O)Cl \xrightarrow[C_2H_4]{} R_3SiOC(O)Cl \xrightarrow{-CO_2} R_3SiCl \quad ,$$
$$(R_3Sn)_2O + COCl_2 \xrightarrow[-R_3SnCl]{} R_3SnOC(O)Cl \xrightarrow{-CO_2} R_3SnCl \quad .$$

Qualitative observations [57-66] have also shown that the replacement of the carbonyl group in the $\equiv Si-O-C(O)-X$ unit by CH_2, $C(CF_3)_2$, SO_2, or PO_2‡ stabilises the molecule as a whole (for example in relation to heating). Subsequent experiments showed that $Me_3SiOC(O)OBu\text{-}n$, $Me_3SiOC(O)OEt$, and $2\text{-}NCOC_6H_4OC(O)OSiMe_3$ [38] evolve CO_2 close to room temperature; $Et_3SiOC(O)OAlk$ and $(Et_3SiO)_2CO$ are slowly decarboxylated during synthesis (105–130°C) and more rapidly at 150–200°C. [39] This implies that silyl carbonates are thermally less stable than silyl *NN*-dialkylcarbamates. For example, $Me_3SiOC(O)NEt_2$ can be boiled for a long time without decomposition at 177–178°C. [68]

It is striking that, on passing from $Me_3SiOC(O)NEt_2$ to $Me_3SiOC(O)N(Et)SiMe_3$, [69] the tendency towards thermal decomposition increases and, of the two systems of conjugated bonds present simultaneously in the latter compound, namely $\equiv Si-OC(O)-X$ [X = $-N(Et)SiMe_3$] and $\equiv Si-N(Et)C(O)-Y$ (Y = $OSiMe_3$), the latter is the more labile:

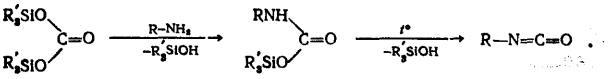


Thus compounds with the $\equiv Si-OC(O)-X$ and $\equiv Si-\underset{|}{N}C(O)-X$ bond systems and in a more general form with $\equiv Si-O-E-X$ and $\equiv Si-\underset{|}{N}-E-X$ (where X is an electronegative group and E a Group II–VIII element) extend Nesmeyanov's classical concept concerning the unusual properties of organoelemental compounds with β-carbofunctional groups and their tendency to undergo β-elimination reactions. These properties are probably characteristic in general of organoelemental compounds with β-functional groups having the general formula $R_{n-1}M^n-E_1-E_2-X$ (where *n* is the valence of the element M and E_1 and E_2 are group II–VIII elements).

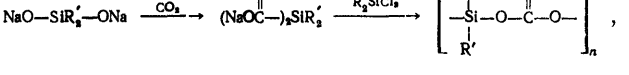
5. Practical Applications

As already mentioned, the silyl carbonates (VI) and (IX) can be used in the synthesis of silyl carbamate esters, aminoacid derivatives, mixed anhydrides of carboxylic and siloxy(alkoxy)carbonic acids, etc. [36] and as mild silylating agents [44], which is extremely important in the study of natural products.

In view of the simplicity with which *O*-silyl carbonates can be obtained, they may serve as a basis for a method of synthesising lower aliphatic isocyanates by a fully phosgene-free method with recycling of the silanol:



The synthesis of poly-(*O*-silyl carbonates) by the phosgene-free method,



is of theoretical interest because, owing to the ease of decarboxylation on acidification, they can be used in the manufacture of polysiloxane foam materials.

‡ The compound $Me_3SiOSeO_2Cl$ may be unstable owing to its insufficient purity. On the other hand, the stability at a high temperature of $Me_3SiOAlCl_3$ (b.p. 226–236°C) [67] and similar derivatives can be accounted for by their existence in an associated form.

III. ORGANOSILICON CHLOROCARBONATES AND CARBONATES WITH CARBOFUNCTIONAL GROUPS

Organosilicon chlorocarbonates with carbofunctional groups are intermediates in the synthesis of silicon-containing mono-, oligo-, and poly-urethanes, a wide variety of carbonates, carbazinic acid derivatives, etc. and for this reason will be considered before carbonates.

1. Methods of Synthesis of Chlorocarbonates

The hydrosilylation reaction of alkenyl (alkenylaryl) chlorocarbonates is remarkable in that it makes it possible to obtain organosilicon chlorocarbonates with one, two, and three carbofunctional groups at the silicon atom, which are important for subsequent chemical reactions [28,29,31,42,70-75]

$$X_nR_{3-n}SiH + >C{=}C-Q-OC(O)Cl \xrightarrow{Cat.} X_nR_{3-n}Si-\underset{H}{\overset{|}{C}}-\underset{|}{C}-Q-OC(O)Cl\ ;$$

X = Cl, OAlk, OSi≡; R = Alk, Ar; Q = alkylene or arylene; $n \leqslant 3$.

Peroxides or Speier's compounds are used as catalysts of the reaction [76]. Its disadvantage is that, in the case of the most readily available compound AllOC(O)Cl§, the addition of hydrosilanes is accompanied by vigorous evolution of CO_2 and propene [77-79] (see also Refs. 76, 80, 81)¶ and the greater part of the initial silane is converted into a more highly chlorinated compound.

The data on the hydrosilylation of AllOC(O)X (where X = H, Cl, OMe, or OAll) [28,29,31,42,70-75] have shown that CO_2 and C_3H_6 are not formed by the reduction of the initial or final chlorocarbonates to unstable formates [82-85] or by the addition of H–Si≡ to the C=O group of the chlorocarbonate with subsequent elimination of siloxy-derivatives via the β-decomposition mechanism. They are produced as a result of double β-decomposition of β-chlorocarbonatopropylsilanes—the products of the addition of H–Si≡ to AllOC(O)Cl in accordance with the Markovnikov rule:

$$\equiv Si-CH(Me)CH_2-OC(O)Cl \xrightarrow[-C_3H_6]{} \equiv Si-OC(O)-Cl \xrightarrow[-CO_2]{} \equiv Si-Cl\ .$$

Furthermore, it has been noted that the hydrosilylation of AllOC(O)Cl is sensitive to the conditions of synthesis [31]. For example, when Speier's catalyst [t-butyl peroxide] is added to the entire reaction mass (A), the yield of the desired chlorocarbonate is low. It increases appreciably when the catalyst and a portion of the mixture of reactants is kept in contact until gas evolution ceases and then the remaining portion of the mixture (B) is added. A mixture (C) of t-butyl and dicumenyl peroxides acts even more selectively in the required direction (see Table).

The reaction of phosgene with organosilicon alcohols and phenols containing carbofunctional groups has been studied in detail since 1965. [24,29-31,42,74,75,86-96]. The reactions with alcohols and glycols proceed vigorously regardless of the position of the hydroxy-group relative to the silicon atom [29,31,42,75,87,89,92] via the mechanism

$$O-\left[-\underset{Me}{\overset{Me}{\overset{|}{Si}}}-R'-OH\right]_2 \xrightarrow{COCl_2} O\left[-\underset{Me}{\overset{Me}{\overset{|}{Si}}}-R'-OC(O)Cl\right]_2 +$$

(XIII) (XIV)

$$+ Cl-\underset{Me}{\overset{Me}{\overset{|}{Si}}}-R'-OC(O)Cl + Cl-\underset{Me}{\overset{Me}{\overset{|}{Si}}}-R'-Cl\ ,$$

(XV) (XVI)

(a) R′=CH_2; (b) R′=$(CH_2)_3$; (c) R′=$(CH_2)_4$; (d) R′=$CH_2O(CH_2)_2$.

Hydrosilylation of allyl chlorocarbonate [31].

Hydrosilane	Method of synthesis and yields of carbonates, %		
	A	B	C
Cl_3SiH	23	62	60
Cl_2MeSiH	24	46	51
$ClMe_2SiH$	22	37	45

The appearance of products (XV) and (XVI) is due to the presence of HCl in the reaction mixture, whose removal by flushing with nitrogen or with the aid of a tertiary amine sharply suppresses side reactions and increases the yield of the required bischlorocarbonates (XIV).

In contrast to alcohols, silicon-containing phenols are inert at moderate temperatures in relation to phosgene. In order to avoid their thermal rearrangement, to phenoxysilanes [30,97] as well as other similar reactions involving the bonds formed by the silicon atom, chlorocarbonates are therefore synthesised in the presence of organic bases, for example [29-31,42,91]:

$$HMe_2SiC_6H_4OH + COCl_2 \xrightarrow[-HCl]{EtN} HMe_2SiC_6H_4OC(O)Cl\ ,$$

(XVII)

$$\left[X-C_6H_3(OH)-R-\underset{Me}{\overset{Me}{\overset{|}{Si}}}-\right]_2O \xrightarrow[-R_3N\cdot HCl]{COCl_2/R_3N} \left[X-C_6H_3(OC(O)Cl)-R-\underset{Me}{\overset{Me}{\overset{|}{Si}}}-\right]_2O\ ;$$

(XVIII) (XIX)

(a) R = single bond and X = H; (b) R = CH_2O and X = Cl; (c) R = $(CH_2)_3$ and X = H.

Treatment of silyl ethers derived from silicon-containing alcohols and phenols with phosgene is in many cases preferable on a preparative scale to the direct reactions of phosgene with the alcohols and phenols discussed above.

Firstly, when the reaction comes to an end, the reaction mixture does not contain the corrosive HCl, instead of which Me_3SiCl, which can be readily removed and which does not cleave the ≡Si–O–Si≡ and ≡Si–O–C≡ bonds, is formed, for example [29-31,86,88,90,91,94,95]:

$$O-\left[-\underset{Me}{\overset{Me}{\overset{|}{Si}}}-(CH_2)_nOSiMe_3\right]_2 \xrightarrow[20-25^\circ C]{COCl_2} O-\left[-\underset{Me}{\overset{Me}{\overset{|}{Si}}}-(CH_2)_nOC(O)Cl\right]_2$$

(XIV)

n=1,3.

Secondly, the advantage of this method compared with the treatment of phenols with phosgene in the presence of HCl acceptors is that the formation of both carbonates and

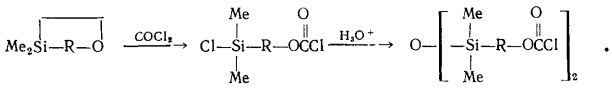
§ Here and henceforth All = allyl.

¶ The evolution of propene during the addition of hydrosilanes to various allyloxy-derivatives was frequently noted also in earlier studies [77-79] and has been described in reviews of the hydrosilylation reaction [76,80,81].

alkylchlorosilanes under the influence of tertiary amines is fully ruled out.

Thirdly, the reaction of $COCl_2$ with alkoxy(alkenoxy, alkynoxy)silanes makes it possible to obtain purely organic chlorocarbonates without HCl, which must usually be removed by special procedures.

The complex (owing to the reversibility of the reaction at high temperatures) stage involving the isolation of organosilicon glycols with carbofunctional substituents (XIII, a–c), (XVIII, b and c), etc. (which are diffiult to obtain in a pure state) during their synthesis from the corresponding silyl ethers (XXI)–(XXIV)†, namely $[-(CH_2)_mOSiMe_2-]_n$ [XXI: (a) $m = 3$, $n = 1$; (b) $m = 4$, $n = 1$; (c) $m = 5$, $n = 1$; (d) $m = 3$, $n \simeq 7-9$; (e) $m = 1$, $n = 2$], o-$C_6H_4OCH_2SiMeO$ (XIII), o-$C_6H_4(CH_2)_3SiMe_2O$ (XXIII), o-$C_6H_4(CH_2)_3SiPh_2O$ (XXIV), etc. is frequently eliminated, because bischloroformates of the disiloxane series can be obtained on a preparative scale by a simpler method involving a combination of the treatment of silyl ethers with phosgene with subsequent hydrolysis of the intermediate monochloroformates:



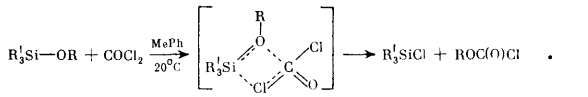
In this connection, it became necessary to investigate in detail the reactivity of the Si–O bonds in various silyl ethers—potential sources of mono- and bis-chloroformates in reactions with phosgene and chloroformates. The reactivity of Si–O bonds in reactions with phosgene depends on many factors and varies within wide limits [31,94]. Thus Me_3Si derivatives of aliphatic alcohols demonstrate a decrease of reactivity: (a) in parallel with the increase in the bulk of the alkyl group: $Me_3SiOMe > Me_3SiOEt \gg Me_3SiOPr\text{-}n > Me_3SiOBu\text{-}n$; (b) on passing to alcohols with a branched structure and to a greater extent the closer the branched site to the reaction centre and the greater the degree of branching: $Me_3SiOPr\text{-}n > Me_3SiOPr\text{-}iso > Me_3SiOcyclohexyl$; $Me_3SiOBu\text{-}n > Me_3SiOBu\text{-}iso > Me_3SiOBu\text{-}s > Me_3SiOBu\text{-}t$.

In the series of trimethylsilyl ether of unsaturated alcohols, the rate of reaction is lower the greater the degree of unsaturation (a): $Me_3SiOPr\text{-}n > Me_3SiOCH_2CH{=}CH_2 > Me_3SiOCH_2C{\equiv}CH$, $Me_3SiOcyclohexyl > Me_3SiOPh$, and the greater the length and degree of branching of the group (b): $Me_3SiOCH_2CH{=}CH_2 > Me_3SiOCH_2CH{=}CHPh > Me_3SiOCH_2C(CH_3){=}CH_2$.

By varying the substituents at the silicon atom, the reactivity of the molecule can also be altered: $CH_2{=}CHCH_2OSiMe_3 > CH_2{=}CH_2CH_2OSiMe_2H$, $MeOSiMe_3 > MeOSiMe_2CH_2Cl$, $Me_3SiOMe > Et_3SiOMe$. Despite the bulky substituents attached to the metal atom, the methoxy-derivatives Et_3GeOMe and $n\text{-}Bu_3SnOMe$ react exothermically with $COCl_2$ and much faster than Me_3SiOMe. Conversely, $Me_3SiOCMe_3$ and $Me_3SiOSiMe_3$, as well as certain other disiloxanes vigorously absorb and retain $COCl_2$, but remain unchanged even on heating [31,94,135]. Me_3SiOMe and Me_3SiOPh are resistant to the action of COF_2 (at 20°C). [55]

† The principal methods for the synthesis of organosilicon alcohols, phenols, silaoxacycloalkanes, etc. can be found in the following publications (including the attached bibliographies): (a) alcohols [26,27,29–31,98–114]; (b) phenols [29–31,110,114]; (c) silaoxacycloalkanes [29–31,113–115].

The nucleophilic substitution of the alkoxy-group in the silanes R^1_3SiOR in a non-polar medium evidently proceeds via an $S_Ni\text{–}Si$ mechanism with formation of a quasi-cyclic transition complex [136]:



Other conditions being equal, the rate of reaction is therefore determined by the nucleophilic properties of $ROSiR^1_3$, which are in this case determined by the overall influence of the inductive and steric effects of the substituents R and R′ and the effect of the (p-d) π-dative interaction via the Si–O bond [137]. Acyloxytrimethylsilanes, where, in contrast to $AlkOSiMe_3$, the lone p electrons of the oxygen atom are involved also in the reverse coordination to the carbonyl oxygen atom: $\equiv Si \leftarrow O\text{—}C(O)R$, therefore exhibit a reduced reactivity. Furthermore, the introduction of electronegative substituents at the silicon atom or the carbonyl group reduces the reactivity of the molecule towards phosgene to an even greater extent [31,94]. For example, acetoxytrimethylsilane reacts faster than $ClCH_2Me_2SiOC(O)Me$, which is in its turn more reactive than $Me_3SiOC(O)CF_3$.

The retardation of the reaction with phosgene on passing from alkoxy- to acyloxy-derivatives can also be followed for germanium and tin compounds, while for acetates of the type $R_3EOC(O)Me$ the rate decreases in the following sequence as a function of E: Sn > Ge > Si [31,94].

The above regularities hold also on treating with phosgene compounds having endocyclic Si–O bonds, although the reaction as a whole acquires a number of new specific features [31]. The main characteristic of such a reaction is that the product of the insertion of $COCl_2$ accompanied by ring opening is formed. The rate of reaction is determined by the size of the heterocycle and the nature of its constituent structural elements. For example [28–31], in the series of silaoxacycloalkanes $Me_2Si(CH_2)_nO$ the rate of ring opening decreases sharply with increase of n: compound (XXIa) ($n = 3$) reacts vigorously even in the cold; although the ring of silaoxacyclohexane (XXIa) ($n = 4$) opens spontaneously, the rate of this process at room temperature is low:

$$Me_2Si(CH_2)_nO + COCl_2 \rightarrow ClMe_2Si(CH_2)_nOC(O)Cl \quad ; \quad n \geqslant 3 \ .$$

The oligomeric macrocyclic product (XXId) ($m = 3$, $n \simeq 7-9$) does not react with $COCl_2$ even at 150°C and only in the presence of catalytic amounts of $ZnCl_2$, $AlCl_3$, $FeCl_3$, etc. is it possible to convert it at 100–130°C into the corresponding chlorocarbonate (XVb), but in a low yield (18%). On the other hand, treatment of the products of the thermal depolymerisation of the oligomer (XXId) with phosgene in the presence of $ZnCl_2$ made it possible to increase the yield of the chlorocarbonate to 60%.

However, catalysts of the type of Lewis acids also have a side effect—they initiate the decomposition of the desired chlorocarbonates to alkyl chlorides. Another group of initiators, whose action is based on the cleavage of the Si–O bonds with formation of a free HO group, was therefore proposed [31,88]: treatment of the HO group with phosgene is accompanied by the evolution of HCl, which maintains the reaction. Inorganic acids or hydroxylated organic compounds are used as initiators of this kind.

The decrease of the reactivity of silaoxacycloalkanes in the sequence (XXId) > (XXIa) > (XXIII) ≫ (XXII) > (XXIII) is caused, as in the case of linear silyl ethers, by the reduced nucleophilic properties of the O atom in the siloxy-group. This happens, for example, on passing from compound (XXIe) to (XXIa), eliminating the influence of the *p* electrons of the second oxygen atom, which competes with the conversion of the Si—O linkage into a double bond. For compounds (XXIII) and (XXIV), the cause is different—the involvement of the *p* electrons of the oxygen atom in conjugation with the aromatic ring. The simultaneous presence in the molecule of compound (XXII) of the epoxy- and siloxyaryl groups or the combination in compound (XXIV) of the $SiOC_{Ar}$ fragment with the bulky phenyl substituents at the silicon atom retard sharply the reactions with $COCl_2$.

Thus the reaction of phosgene with silyl ethers, which are intermediates in the synthesis of glycols and bisphenols of the siloxane series, is of preparative value for derivatives of alcohol and is of limited value in the case of a compound with a $Si-OC_{Ar}$ linkage.

The reaction of phosgene with epoxysilanes is of interest as an independent method for the synthesis of organosilicon chlorocarbonates[71]:

$$\equiv Si(CH_2)_3OCH\!-\!CH_2 + COCl_2 \rightarrow \equiv Si(CH_2)_3OCH(Cl)CH_2OC(O)Cl \quad ,$$

a distinctive feature of which is the complete absence of side products.

2. Methods of Synthesis of Carbonates

The hydrosilylation of alkenyl carbonates is used to obtain monomeric, oligomeric, and polymeric products containing simultaneously the carbonate and organosilyl groups[29,31,138–145]. The reaction was described for the first time by Haluska in 1976:[138,141,143,144]

$$ROC(O)OA \xrightarrow[H_2PtCl_6]{} \begin{cases} \xrightarrow{HSiR'_nX_{3-n}} ROC(O)OR''SiR'_nX_{3-n} \\ \xrightarrow{HSi(R'_n)O_{(3-n)/2}} ROC(O)OR''Si(R'_n)O_{(3-n)/2} \end{cases} ;$$

R = Alk or Ar; A = alkenyl, n = 1-3; X=OC(O)Me, NMe_2, $ON{=}CMe_2$ etc.

However, since the course of the reaction is treated as unambiguous even in those cases where the initial compounds contain functional groups chemically reactive relative to one another, for example:

$$\equiv Si-H + HOSi \equiv \rightarrow H_2 + \equiv SiOSi \equiv \quad ,$$
$$\equiv Si-H + CH_2{=}CHSi \equiv \rightarrow \equiv SiCH_2CH_2Si \equiv \quad .$$

the above scheme cannot be regarded as correct. It has been shown[31,145] that the formation of equimolar amounts of CO_2, C_3H_6, and the corresponding methoxysilanes in addition to γ-adducts (40–60%) is observed in the hydrosilylation of AllOC(O)OMe. Such proportions of the products of the accompanying reactions have been interpreted as evidence for the formation of unstable β-adducts, which decompose via a double β-decomposition mechanism:

$$\begin{matrix} O\!-\!Me \\ | \\ O\!=\!C \\ | \\ O\!-\!All \end{matrix} \xrightarrow[H_2PtCl_6]{R_nCl_{3-n}SiH} \begin{cases} \longrightarrow MeOC(O)OCH_2CH_2(Me)Si \equiv \xrightarrow[2.\ -CO_2]{1.\ -C_3H_6} MeOSi \equiv \\ \longrightarrow MeOC(O)O(CH_2)_3Si \equiv \end{cases}$$

R=Me, Et, or Ph; n = 0 — 3.

Tetramethyldisiloxane and AllOC(O)X (where X = OMe or H) react stepwise via both Si—H bonds, the main and side reactions leading respectively to symetrically and asymmetrically substituted disiloxanes:

$$O\!-\!\left[\begin{matrix} Me \\ | \\ -Si(CH_2)_3OC(O)X \\ | \\ Me \end{matrix}\right]_2 \qquad \begin{matrix} Me\ Me \\ | \quad | \\ X\!-\!SiOSi(CH_2)_3OC(O)X \\ | \quad | \\ Me\ Me \end{matrix} .$$

A general feature of the hydrosilylation of the allyl ethers AllOC(O)X (where X = H, OMe, OAll, or Cl) by hydrosilanes of the same type is a decrease of the fraction of side products as a function of the nature of the group X in the sequence Cl > OMe > H > OAll. For example, diallyl carbonate reacts with hydrosilanes like AllOC(O)OMe, but the liberation of gaseous products in side reactions is observed to a lesser extent, the yield of product (XXV) increasing with increase of n from 56 to 76%:[31,145]

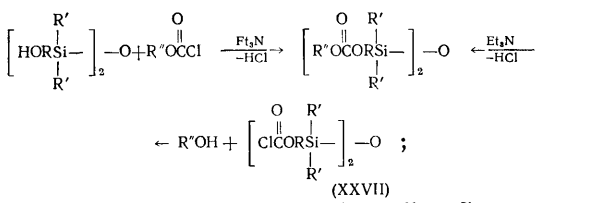
$$Cl_nMe_{3-n}SiH + (AllO)_2CO \rightarrow [Cl_nMe_{3-n}Si(CH_2)_3O]_2CO \quad ;$$
$$n{=}1-3 \quad .$$
(XXV)

On the other hand, the yield of reaction products diminishes for each AllOC(O)X on passing from Cl_3SiH (n = 3) to less chlorinated hydrosilanes. The tendency towards a decrease of the yield of silyl carbonates with accumulation of alkyl radicals in the initial silane is manifested most clearly by Et_3SiH: approximately 14% of the hydrosilane is consumed in the formation of the main product, while the remainder is involved in side reactions with formation of β-adducts, detected as the products of their β-decomposition, for example, $Et_3SiOSiEt_3$ and $Et_3Si(CH_2)_3OSiEt_3$.[31,145] Theoretically, these compounds might be formed together with CO_2 and propene via the mechanism of the reaction of hydrosilanes and organic carbonates discussed above[39,40]. However, experiments failed to confirm this hypothesis, because the reaction products do not contain Et_3SiPr-n and Et_2SiPr-iso, which should have been inevitably formed together with the main products.

Treatment of organosilicon alcohols and phenols with phosgene leads to symmetrical carbonates if the process does not stop at the stage involving the formation of chlorocarbonates (see Section III, 1). In view of the difficulty of replacing the second chlorine atom in phosgene by an ester group, the reaction is carried out in the presence of organic bases[29–31,42,92,146], for example:

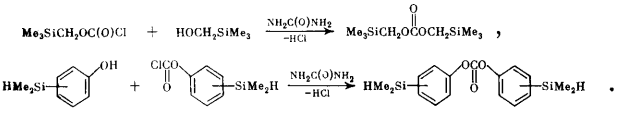
$$HMe_2SiC_6H_4OH + COCl_2 \xrightarrow{Et_3N} (HMe_2SiC_6H_4O)_2C{=}O \quad .$$
(XXVI)

The reactions of chloroformates with alcohols and phenols lead to symmetrical and asymmetric carbonates with the silicon atom in one or both organic groups [34,138,141,143,144,147-150], for example:



(XXVII)

R=$(CH_2)_3$, $(CH_2)_4$, or $(CH_2)_3OCH_2CH(Me)$; R′=Me or Ph; R″=Me, n-Bu, Cl_3C, or All.



The heterofunctional condensation reaction with participation of siloxy-derivatives and chlorocarbonates makes it possible to obtain organic and organosilicon carbonates and polycarbonates [31,42,55,95]. Compared with phosgene, aliphatic and aromatic chlorocarbonates are less reactive in relation to silyl ethers derived from alcohols and phenols. The reaction proceeds at an appreciable rate only at a temperature of the order of 120–220°C even for alkoxytrimethylsilanes which are most readily cleaved by phosgene:

$$\equiv Si{-}OR + ClC(O)OR' \xrightarrow{t} \equiv Si{-}Cl + ROC(O)OR' \quad .$$

As in the case of $COCl_2$, the $\equiv Si{-}OC_{Ar}$ bond is less reactive than $\equiv Si{-}OC_{Alk}$. On the other hand, the surprising inertness of 1,3-bis(trimethylsiloxymethyl)-1,1,3,3-tetramethyldisiloxane in relation to the bischlorocarbonates (XIVa) and (XIVb) may be a consequence of the steric effect of the Me_3Si group and the stronger (p-d) π-interaction via the linkage

$$Me_3Si\overset{\curvearrowleft}{\ddot{O}},$$

due to the influence of the second organosilyl group, which usually increases the electron density at the heteroatom in the α-position [114].

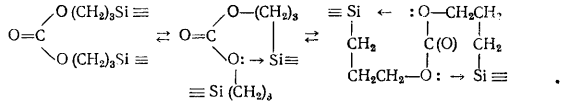
It is of interest that fluorocarbonates are more reactive than chlorocarbonates [55]: ROC(O)F (R = Et, n-Pr, or n-Bu) reacts with $Me_nSi(OR)_{4-n}$ (n = 2, 3) even at 0–20°C with formation of the corresponding carbonates [55].

3. The Properties of Organosilicon Chlorocarbonates and Carbonates with Carbofunctional Groups

The available data on the chemical reactions of organosilicon chlorocarbonates and carbonates with carbofunctional groups and their physicochemical properties are fairly extensive and have already been partly surveyed [31]. They make it possible to isolate a number of properties distinguishing this group of compounds from their purely organic analogues.

(a) Infrared spectra. The ν(CO) band in the infrared spectra of chlorocarbonates and acetates is located respectively in the ranges 1775–1783 and 1739–1786 cm^{-1}. The absorption by the carbonyl group in the formates $R_2Si(CH_2)_3OC(O)H$, where R_3Si = Cl_3Si, Cl_2MeSi, $ClMe_2Si$, Et_3Si, $PhCl_2Si$, $(EtO)_3Si$, or $HC(O)OSiMe_3-OSiMe_2$, and in the carbonates $R_3Si(CH_2)_3OC(O)OMe$ and $R_3Si(CH_2)_3OC(O)O(CH_2)_3SiR_3$, where R_3Si = Cl_3Si, Cl_2MeSi, $ClMe_2Si$, Et_3Si, Cl_2PhSi, $(EtO)_3Si$, $Me_2(MeO)Si$, or $Ph(EtO)_2Si$, is constant for each series and almost independent of the substituents at the silicon atom: the absorption band in the spectra of the formates is located in the range 1720–1722 cm^{-1} and that in the spectra of the carbonates is in the range 1748–1752 cm^{-1}. Comparison showed that, in the series of compounds $\equiv Si(CH_2)_3OC(O)H$, $\equiv Si(CH_2)_3OC(O)OMe$, and $\equiv Si(CH_2)_3OC(O)Cl$, the absorption band is displaced towards shorter wavelengths with increasing electronegativity of the substituent at the carbonyl carbon atom (Cl > OMe > H).

The appearance of a doublet in the region of the ν(CO) absorption in the spectra of the dicarbonates may be caused by reversible intramolecular coordination:



(b) ^{1}H NMR spectra. Analysis of the integrated spectra for the stable forms of organosilicon chlorocarbonates, carbonates, formates, and intermediate acetates having the general formula $Cl_nMe_{3-n}SiC_3H_6OC(O)X$ (X = H, Cl, OR, or Me), synthesised in different ways, confirms the structure with the trimethylene bridge between the silicon atom and the functional group [28,31,72,73,145].

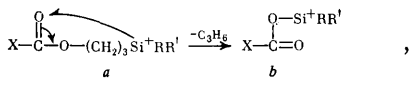
The deshielding influence of the silyl group is a maximum for Si-methylene protons, decreasing with increase of the number of alkyl groups at the silicon atom and decaying rapidly along the chain. The influence of the nature of the substituent X on the $\equiv SiCH_2$ group varies unambiguously both on passing from formates to carbonates and chlorocarbonates for the same silyl substituent and when the silyl group $ClMe_2Si$ is replaced by Cl_2MeSi and Cl_3Si keeping X unchanged. For the protons of the β- and γ-methylene groups, the influence of the silyl and X groups is more complex.

Comparison of the chemical shifts of the protons in the $(CH_2)_3$ group in the series of carbonates $(Cl_nMe_{3-n}SiCH_2.)_2CO$ shows that, on passing from asymmetric to symmetrical carbonates, the deshielding influence of similar silyl groups on the protons in the α- and β-positions relative to the silicon atom diminishes. A decrease is also observed in the degree of deshielding of the β-protons, the deshielding differing appreciably from the approximately constant value for mono-, di-, and tri-chlorosilyl derivatives of asymmetric carbonates. On the other hand, the tendency towards a decrease of the degree of partial dissociation of γ-protons in the series of $ClMe_2Si$-, Cl_2MeSi-, and Cl_3Si-substituted asymmetric carbonates is replaced by the opposite tendency for the symmetrical analogues.

(c) Mass spectra‡. The following features were observed in the study of the mass spectra of the organosilicon formates $R'R_2SiCH_2CH_2CH_2OC(O)H$ [where $R'R_2Si$ = Me_2ClSi, $MeCl_2Si$, Cl_3Si, $PhCl_2Si$, $(EtO)_3Si$, Et_3Si, etc.]

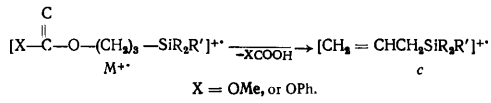
‡ For a comparison of the mass spectra of organic carbonates, see Brown and Gunther [152].

and methylorganosilyl carbonates of the type $R'R_2Si(CH_2)_3.OC(O)OMe$ [where $R'R_2Si = Cl_3Si$, $MeCl_2Si$, Me_2ClSi, $(EtO)_3Si$, Et_3Si, $MeOMe_2Si$, etc.][31,151]: (a) there are no molecular ion peaks; (b) the peak of the Si^+R_2R' ion has the maximum intensity in all cases, except for the formate with the $(EtO)_3Si$ substituent. The intensities of the $a(M-R)^+$ and $a'(M-R')^+$ ions are low. These ions are sometimes altogether absent. However, the $b(a-C_3H_6)$ and $b'(a'-C_3H_6)$ ions formed via the mechanism



were always observed. This is the mechanism of the rearrangement of trimethylsilylcarboxylic acid esters and chlorides[153,154].

A second characteristic pathway in the decomposition of organosilylcarbonates under the influence of electron impact involves the loss of X–COOH molecules and the formation of the ions c:

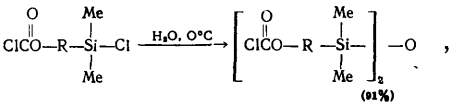


X = OMe, or OPh.

The relative contribution of the decomposition to the ion b or the ion c depends on the nature of the substituents at the silicon atom: with increase of the number of Cl atoms, the contribution of the pathway leading to the ion a increases.

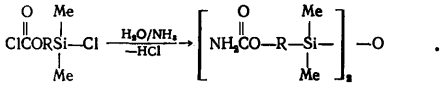
The mass spectrum of $(Me_3SiCH_2O)_2CO$ contains peaks due to the molecular ion with m/e 234 and the $(M-CH_3)$ ion typical for Me_2Si derivatives with m/e 219.

(d) Chemical properties. Organosilicon chlorocarbonates and carbonates may react via the C- and Si-functional centres both separately and simultaneously. Thus hydrolysis of the chlorocarbonates $ClMe_2SiROC(O)Cl$ by ice water leads to the corresponding bischlorocarbonates[28,31,42,86]:

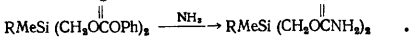


(91%)

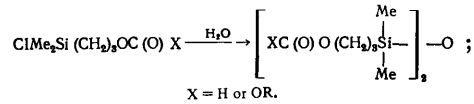
while treatment with aqueous ammonia converts them into the corresponding biscarbamates[28,31,42,75,86,89]:



The latter reaction actually constitutes the specific synthesis of organosilicon carbamates and biscarbamates, which Fessenden and Coon[148,149] obtained by the ammonolysis of the corresponding carbonates and biscarbonates:

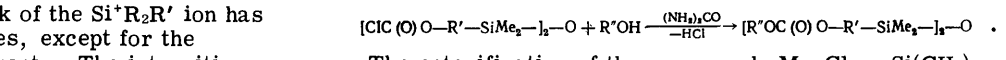


Formates and carbonates are hydrolysed similarly to chlorocarbonates[31,72,145]:

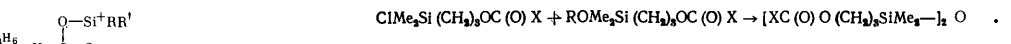


X = H or OR.

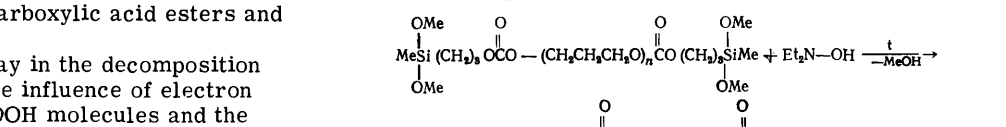
Chlorocarbonates and bischlorocarbonates react with alcohols and phenols to form carbonates and biscarbonates[29–31,91]:



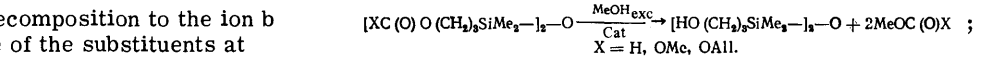
The esterification of the compounds $Me_nCl_{3-n}Si(CH_2)_3.OC(O)X$ (X = H, Cl, or OR) is accompanied by heterofunctional condensation[31,145] via Si–Cl and Si–OR bonds, for example§:



When $Me(MeO)_2Si$-substituted polyoxyalkylene dicarbonates are treated with *NN*-dialkylhydroxylamines, methanol is displaced[140]:

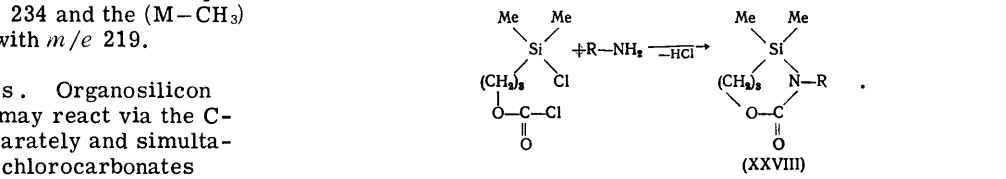


In the presence of toluene-*p*-sulphonic acid or acid ion-exchange resins, organosilicon carbonates are transesterified by the excess methanol, like the acetates and formates[31,72], for example:



X = H, OMe, OAll.

Mono- and bis-chlorocarbonates react with ammonia and organic amines to form carbamates, for example:[28,30,42,89,92,155]

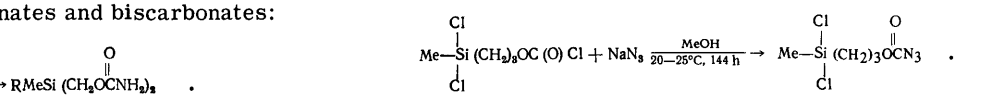


(XXVIII)

Bischlorocarbonates react with hydrazine, aliphatic dihydrazines, acylhydrazines, and diamines in the presence of HCl acceptors to form oligourethanes[31,32,156–160]. It is more convenient to *N*-silylate polyamines in this reaction¶, since the necessity for the removal of corrosive hydrogen chloride and ammonium salts is then obviated[31,32,157].

A similar principle holds in the synthesis of carbonates and polycarbonates, where it proved more convenient to use the silyl ethers derived from alcohols and phenols (rather than the latter themselves) in the reaction with chloroformates[31,96,164] (see below) and in the synthesis of oligosiloxanes with terminal anhydride groups[27], for example from trimellitic acid chloride.

Chlorocarbonates react with alkali metal azides to form the corresponding azidocarbonates[70,71]:



§ Disiloxane may also be formed owing to the presence of H_2O formed by the reaction MOH + HCl → MCl + H_2O.

¶ The reactivity of the Si–N bonds in various aminosilanes in relation to organic chlorocarbonates has been studied[161,162].

In the presence of an organic base, t-BuOOH esterifies chlorocarbonates like alcohols [165]:

$$(MeO)_3Si(CH_2)_3OC(O)Cl + HOOBu\text{-}t \xrightarrow[0°,\ 3\ h]{Py,\ Et_2O} (MeO)_3Si(CH_2)_3OC(O)OOBu\text{-}t.$$

The specific synthesis of this peroxide consists in the hydrosilylation of AllOC(O)OOBu-t in the presence of Speier's catalyst [165]:

$$(MeO)_3SiH + CH_2=CHCH_2OC(O)OOBu\text{-}t \xrightarrow[3\ h]{50°C} (MeO)_3Si(CH_2)_3OC(O)OOBu\text{-}t.$$

Bis(organosilylalkyl)-substituted percarbonates have been synthesised from organosilicon chlorocarbonates and hydrogen peroxide [166]:

$$(MeO)_3Si(CH_2)_3OCCl + HOOH \xrightarrow[10°C]{Py} (MeO)_3Si(CH_2)_3OC(O)O-O-C(O)(CH_2)_3Si(OMe)_3 .$$

The chlorocarbonate $Me_3Si(CH_2)_3OC(O)Cl$ and its organic analogues [167] can be converted into the corresponding aldehydes [31,95]:

$$Me_3Si(CH_2)_3OCCl \xrightarrow{DMSO} \left[Me_3Si(CH_2)_2CH_2-O-\overset{\overset{Me}{|}}{\underset{\underset{Me}{|}}{S}}=O\right]Cl^- \xrightarrow[CO_2]{Et_3N} Me_3Si(CH_2)_2C(O)H.$$

However, the sulphoxonium salt derived from $Me_3SiCH_2OC(O)Cl$ forms $ClCH_2SiMe_3$, which is probably due to the enhanced basicity of the oxygen atom in the α-position relative to the Me_3Si group:

$$\left[Me_3Si-CH_2-O-\overset{\overset{Me}{|}}{\underset{\underset{Me}{|}}{S}}=O\right]Cl^- \xrightarrow[-CO_2]{Et_3N} [Me_3SiCH_2OSMe_2]Cl^- \xrightarrow{-Me_2SO} Me_3SiCH_2Cl .$$

It is also extremely significant that the steric effect of the Me_3Si group prevents the abstraction of a proton under the influence of Et_3N.

(e) Practical importance. It is seen from the foregoing that chlorocarbonates are used to synthesise mono- and bis-carbonates, mono- and bis-carbamates, mono- and bischlorocarbonates, azidocarbonates, organosilicon peroxides, alcohols, diols, aldehydes, heterocyclic compounds, etc. Bischlorocarbonates serve as the basis for the synthesis of silicon-containing polyurethanes and polycarbonates. Positive results have been obtained when carbonates and formates were used as vulcanising agents in the cold hardening of silicon rubbers [31]. Polysiloxanes with carbonatoalkyl(aryl) substituents in the side chains, at the ends of the chains, or in the main polymer chain are obtained from mono- and bis-carbonates with hydrolysable groups at the silicon atom.

All these examples of the practical employment of carbonates are considered in detail in Sections IV and V.

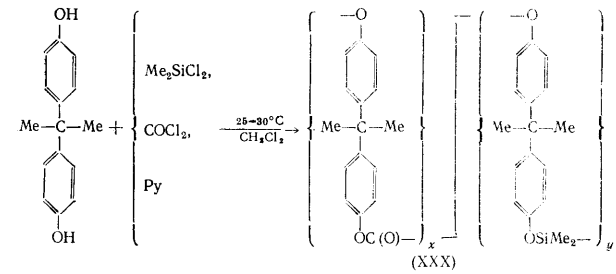
IV. SILICON-CONTAINING POLYCARBONATES

The overall group of silicon-containing polycarbonates (SCPC) includes statistical copolymers, block copolymers, and other compositions.

1. Methods of Synthesis

The SCPC are obtained by treatment with phosgene, transesterification, hydrosilylation, radical polymerisation, and other methods.

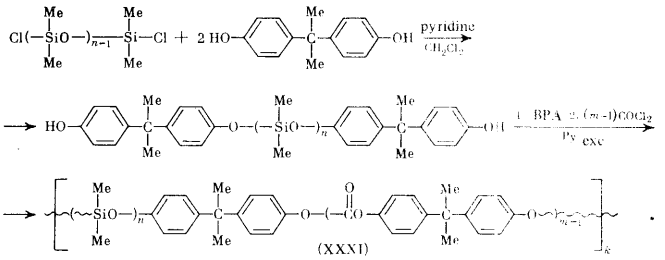
(a) Treatment with phosgene. Two procedures have been proposed for the synthesis of SCPC: firstly, by replacing parts of the phosgene in the treatment of bisphenol A (BPA) with the latter in pyridine by dichlorodimethylsilane (DCDMS), copolymers (CPL) containing bisphenol-carbonate and bisphenol-siloxy-groups were obtained [168-170] (Goldberg's method):



(XXX)

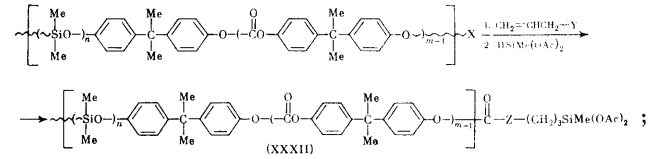
In the second version of the synthesis, an oligocarbonate with $\alpha\omega$-hydroxy-groups is obtained and made to react with DCDMS in the presence of pyridine [168]. When Me_3SiCl is present in the reaction mixture, organic polycarbonates with terminal Me_3SiO groups are obtained [171].

However, these procedures have found only limited applications [172-175] and were subsequently modified [176-203]. Siloxane-carbonate block copolymers, used to make gas-separating membranes, have now been synthesised by the modified method. The modification involves the replacement of DCDMS by an oligosiloxane with terminal Si–Cl bonds (Vaughn's method), which makes it possible to obtain a copolymer with a predetermined content of siloxane blocks whose size is known beforehand [176,180,188,195]:



(XXXI)

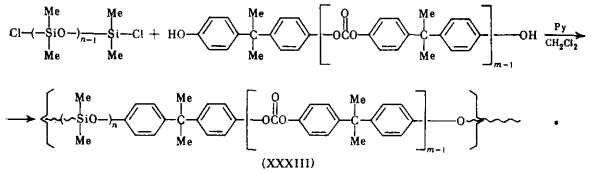
A logical development of this research was a method for the synthesis of block copolymers of type (XXXI) with terminal hydroxy (in the presence of an excess of BPA) or chlorocarbonate (in the presence of an excess of $COCl_2$) groups. After treatment with AllNCO in the former case and with AllOH or allylphenol in the latter, the products are forepolymers capable respectively of being hardened either directly or after hydrosilylation, for example with diacetoxymethylsilane [177,178,184,185,187]:



(XXXII)

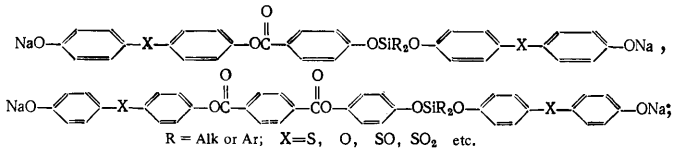
(a) X = OH, Y = NCO, Z = NH; (b) X = C(O)Cl, Y = OH, Z = O .

A variety of this method consists in the copolycondensation of a $\alpha\omega$-dichloropolydimethylsiloxane oligomer with a BPA-carbonate oligomer[197]:



(XXXIII)

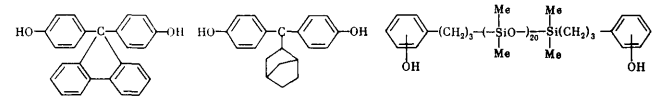
The synthesis of SCPC by treating aryloxysilanes of the type



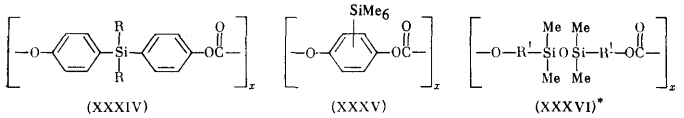
R = Alk or Ar; X=S, O, SO, SO_2 etc.

with phosgene has been reported[204].

In the vast majority of studies, BPA or tetrachloro-BPA is used as the bisphenol in the synthesis of SCPC by the above method, while hydrogen chloride is bound by pyridine. The compounds

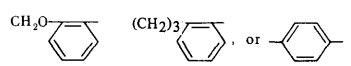


etc. have been recently proposed[186,205] as the dihydroxy-compounds and pyridine has been replaced by NH_3 [182] or alkali metal hydroxides[181]. Dichloromethane is a generally used solvent in the stage involving treatment with phosgene. The copolymers are obtained in a pure form by precipitation from solutions with lower alcohols. In all the studies enumerated, polymers were obtained with an Si–OAr bond susceptible to hydrolysis. In order to eliminate this disadvantage, a study was made of the treatment with phosgene of organosilicon diols and bisphenols containing carbofunctional groups and a fundamentally new set of SCPC [(XXXIV),[206,207] (XXXV),[208] and (XXXVI)[31,96,116,209]] was obtained:



(XXXIV) (XXXV) (XXXVI)*

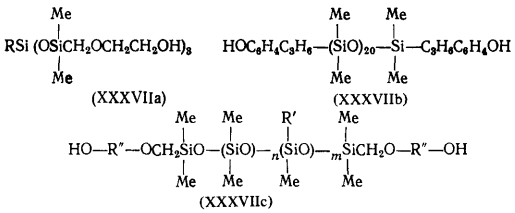
R = Me or Et; R' = (CH_2), $(CH_2)_3$, $CH_2O(CH_2)_2$, $CH_2S(CH_2)_3$,



Apart from the direct treatment of dihydroxy-derivatives with phosgene, modified syntheses of SCPC have been carried out: (a) with partial replacement of the silicon-containing diol or bisphenol by BPA or 1,1-bis-(4-hydroxyphenyl)-cyclohexane (BHPC),[31,96] (b) with partial replacement of $COCl_2$ by silicon-containing bischlorocarbonates with carbofunctional groups[31,96], and finally (c) with complete replacement of $COCl_2$ by a mixture of organic and organosilicon bischlorocarbonates† [164,210].

† Dihydroxy-derivatives with R = $CH_2O(CH_2)_2$, $CH_2S(CH_2)_3$, $CH_2O-C_6H_4$, etc. are considered in this section in view of the similarity of their properties with organosilicon diols and bisphenols containing other carbofunctional groups.

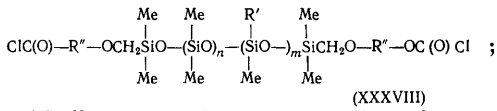
In many cases, oligosiloxanes containing hydroxyalkyl and hydroxyaryl substituents at the silicon atom are used in order to increase the content of siloxy-units in the SCPC:[23-27,164,187,205,211]



(XXXVIIa) (XXXVIIb)

(XXXVIIc)

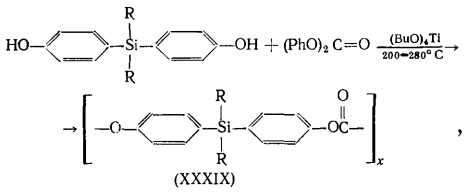
or the corresponding bischlorocarbonates (XXXVIII) are employed, for example[164,210]:



(XXXVIII)

a) R=Me, $m = 0$, $n = 10$; (b) R = vinyl, $n = 6$, $m = 2$; (c) R=Me, $n = 56$, $m = 0$; (R'' = $-CH_2OCH_2CH_2-$) throughout.

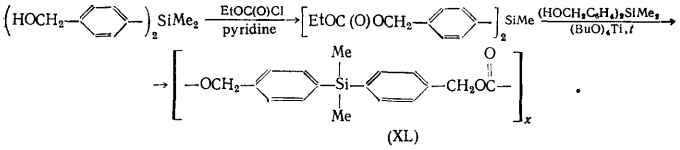
(b) Esterification, hydrolytic, etc. reactions. SCPC are obtained by the transesterification of organic carbonates[206,207] by organosilicon dihydroxy-compounds:



(XXXIX)

where R = Me or Et.

It has been shown[150] that silicon may be present in both initial reactants:



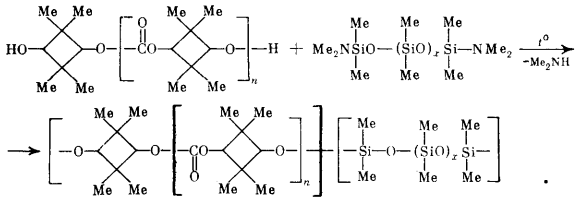
(XL)

It is of interest that compounds of the type Ph_4Si and $Ph_2(EtO)SiH$ are used as catalysts of the reaction of carbonic acid esters with aromatic dihydroxy-compounds both separately, in combination with one another, or in mixtures with alkali metal fluoroborates[212-214]. Presumably they are involved in dehydrocondensation, esterification, and transesterification reactions and probably form part to some extent of the composition of the final polymer in a chemically combined form.

Block copolymers based on a polycarbonate (PC) with terminal $\alpha\omega$-hydroxy-groups and an organopolysiloxane (PS) with 2–4% of Si–OH groups are obtained by heating the initial components in tetrahydronaphthalene at its boiling point. The initial mixture can also include a polyester based on a mixture of tris(hydroxymethyl)propane with ethylene glycol and dimethyl terephthalate. In the latter case, tolylene di-isocyanate or its adduct with tris(hydroxymethyl)propane is added in order to harden varnish compositions, for example[215,216].

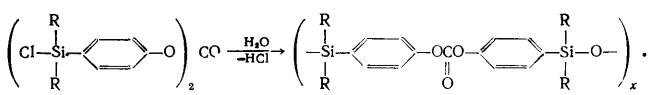
Polyoxyalkylene (POA) with a terminal carbonate group and PS blocks may be linked chemically in the presence of the corresponding combinations of functional groups in pairs (≡Si–H/alkenyl, ≡Si–H/HOC–, and ≡Si–OAlk/HO–C≡) by hydrosilylation, dehydrocondensation, and transesterification reactions[217-222]. It has been reported that αω-$(HO)_2$-PC esterify αω-Cl_2-PS in the presence of a tertiary amine, after which the copolymer is made to undergo heterofunctional polycondensation with $MeSi(OAc)_3$ via the ≡Si–Cl groups introduced in excess[223, 224].

However, the method of synthesis of SCPC based on the interaction of αω-$(Me_2N)_2$-PS and αω-$(HO)_2$-PC, carried out in a homogeneous medium with formation of the readily removed volatile dimethylamine, has attracted more attention[218,220,221]:



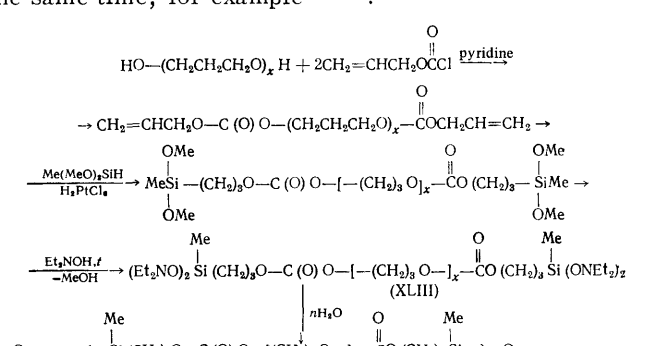
(XLI)

Hydrolysis of organosilicon carbonates containing carbofunctional substituents with participation of the functional groups at the silicon atom is a general method for the synthesis of organopolysiloxanes containing carbonate groups in the polymer side chain, for example[138,143,144,146,216,225]:



(XLII)

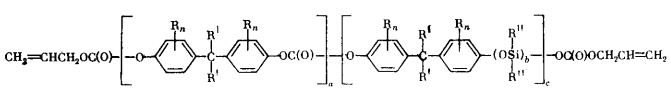
(c) The hydrosilylation reaction. This reaction has a wide scope in the synthesis of SCPC.[139,140,142,177,178,185,218,219,225-231] Its main purpose is to link together the organic and organosilicon components of the polymer. However, the no less important problem of imparting to the adduct the capacity for being vulcanised via the simplest possible scheme is frequently solved at the same time, for example[142,230]:



(XLIII)

(XLIV)

(d) Radical polymerisation. Copolymeric organopolysiloxane-polycarbonates with terminal allyl carbonate groups[139,140,142,177,178,185,228-231]



are mixed with an organosilicon dithiol selected from a group of compounds of the type $[HS(CH_2)_3]_2SiMe_2$, $[HS(CH_2)_n]_2SiMeEt$, and $[HS(CH_2)_3SiMe_2]_2O$, a suitable solvent is added (ethyl methyl ketone, CH_2Cl_2), and the system is hardened by irradiation with light in the range 100–20 000 Å at 0–50°C. Vulcanisation takes place as a result of the addition of HS groups to the double bonds[232].

The introduction of a polysiloxane containing vinyl groups has a favourable effect on the properties of the copolymer of diallyldiglycol carbonate and methyl methacrylate. The copolymerisation is carried out in the presence of peroxide catalysts or under the influence of ultraviolet light[233]. The possibility of the copolymerisation of a BPA-based polycarbonate with an unvulcanised silicon rubber in the presence of kaolin (filler), a naphthalene plasticiser, hydroquinone, and a mixture of benzoyl and t-butyl peroxides has been demonstrated[234]. For example, organosiloxane elastomers are obtained by the interaction of the mixture obtained on copolymerising $(Me_2SiO)_4$ and $(MeVinSiO)_4$, SiO_2, $Ph_2Si(OH)_2$, and the ester $[BuOCH_2CH_2OC(O)OCH_2CH_2]_2O$ containing a carbonate group in the presence of benzoyl peroxide or on heating[235].

Organic percarbonates and organosilicon percarbonates with carbofunctional groups are used for the vulcanisation of polysiloxane materials[165,236-240].

(a) Other compositions based on silicon-containing polycarbonates. Complex compositions incorporating a wide variety of components and containing both a carbonate group and a silicon atom are known. The effective operational characteristics of these compositions are sometimes retained for a long time, although chemical bonding between the components is either not evident or absent altogether. For example, in order to increase the ultimate strength of plastic lubricants, the latter are thickened with finely dispersed amorphous SiO_2 and C_2–C_{18} alkylene carbonate is added as the dispersing agent. The resulting lubricant has a penetrability of 251 and can be used successfully at high temperatures[241]. $(SiO)_n$ (n = 1, 2) can form part of the composition based on a high-molecular-weight linear polycarbonate[242].

Polycarbonate-siloxane compositions, which do not adhere to the mould during compression moulding or casting, are obtained by combining an aromatic polycarbonate with solid crystalline phenylcyclosiloxanes[243]. The introduction of a polysiloxane into a polycarbonate is carried out in mixers of the usual type, for example, in a screw-conveyor granulator[243]. The introduction of a polysiloxane into a polycarbonate lowers the viscosity of the melt, increases its resistance to the action of moisture, and reduces its adhesion to the surfaces with which it is in contact and thereby facilitates its processing by pressing, casting under pressure, extrusion, and other methods[235,243-248]. The addition of a polysiloxane and 0.1–2.0% of an alkali or alkaline earth metal carbonate to a polycarbonate also ensures a high resistance of the composition to the action of light at an elevated temperature[249].

The intermediate formation of silyl carbonates is possible during the hardening of αω-Cl_2-PS with the aid of a mixture of $CaCO_3$, SiO_2 of type U-333, $(EtO)_4Si$, and ethanolamine[250,251] and also in the preparation of moulded foam silicate articles with the composition thickened before foaming (when liquid sodium glass is treated with organic chlorocarbonates as the gel-forming agents)[252].

Silicon may be introduced into the composition of carbonate-containing articles by employing organosilicon compounds as surface-strengthening agents or binders [253-257]. It is also introduced into polycarbonate compositions together with glass fibre (frequently employed for reinforcement [10,11,230,258-261]), silicon carbide [230], and magnesium silicate [262]. In order to modify their surface properties, polycarbonate articles are coated by a solution of an organopolysiloxane with functional substituents [263].

SCPC compositions have been developed in which one of the components is a polycarbonate or poly(vinyl chloride), while the second component is a polycarbonate containing at least one organic substituent with an imide group [264]. Silicon compounds are effective stabilisers of the properties of polycarbonates. For example, the addition of 0.002–0.005% of a high-molecular-weight linear polysiloxane to a polycarbonate makes it possible to obtain homogeneous transparent films. The fibre-forming properties of polycarbonates are improved at the same time [245]. The introduction of 0.1–25.0% of organosilicon halogen-containing compounds into polycarbonate compositions imparts to the latter thermal stability, capacity for internal plasticisation, and self-quenching properties [265].

In order to stabilise the colour of the polycarbonate during its processing, ultramarine and triphenyl or trihexyl-silane are added in amounts of 0.1 and 0.01% respectively [266]. Instead of compounds of the type R_3SiH, it is possible to use for this purpose a polysiloxane, for example, methylphenylpolysiloxane, or SiO_2 with a hydrophobic coating [267]. Polycarbonates stabilised in this way are resistant to the action of atmospheric moisture, heat, solvents, and wear.

It is believed that the hardening of $\alpha\omega$-Cl_2-PS is accelerated in the presence of ammonium carbonate and bicarbonate [268], guanidinium carbonate [269], $(HOCH_2CH_2.NMe_3)_2CO_3$, [236] and Group I, II, and VIII metal carbonates [140,178,205,217,229,230,249-251,271-279].

2. Physicochemical Properties of SCPC

The physicochemical properties of SCPC must be considered separately for polysiloxane-polycarbonate block copolymers and similar compounds, SCPC based on organosilicon monomers with carbofunctional groups, and other types of mixed compositions.

(a) Properties of polycarbonates with ≡SiOCAr linkages. Conditions have been found for the preparation of polycarbonates with ≡SiOCAr linkages in the form of single crystals and their physical properties have been investigated [170-175,193-204,260,279-285]. It has been established that the single crystals of SCPC block copolymers have a hexagonal unit cell [197,199], in contrast to BPA-PC and PDMS, which crystallise with a helical structure containing unit cells of the orthorhombic and monoclinic types respectively [281,282].

The changes in the mechanical, optical, and dielectric characteristics of the block copolymers have been studied in detail as a function of the size and the relative contents of the polycarbonate and polysiloxane blocks in the macromolecule [170-175,193-204,260,279,280]. The study of the equilibrium swelling of SCPC specimens having different compositions, swelling as a function of the deforming stress and deformation frequency, small- and large-angle X-Ray scattering, double refraction, and optical dichroism for block copolymers in the swollen and solvent-free states established that there is a distinct tendency towards the association of the polycarbonate blocks into discrete randomly distributed domains. According to X-ray diffraction and electron microscope data, the average distances between the domains are 50–500 Å. [196,201] It has been established that the dielectric losses of the copolymers with short blocks are greater than for those with large blocks [285]. At the same time, the strength of the block copolymer films increases with increasing content of polycarbonate units and the elongation coefficient diminishes correspondingly [195]. With increase of the content of siloxy-groups in copolymers, the softening temperature falls and the intrinsic viscosity decreases [170,172-175].

The thermal decomposition of SCPC begins to develop at an appreciable rate at 350°C owing to the rupture of the ≡Si–O–C≡ linkages. The ultimate tensile strength of the polymer at 100°C is lower by a factor of two than at 20°C. Cooling to −150°C is accompanied by the brittle rupture of the film specimens [174,175]. At the air–water interface, the block copolymers form a monolayer comprising polysiloxane blocks, while the polycarbonate blocks protrude above the interface [193,198]. The surface activity of mixtures of BPA-based polycarbonates and block copolymers deposited in the form of thin, strong films on glass was studied by determining the wetting angles by means of a telescope having a low resolving power and fitted with a goniometer eyepiece [200]. The wetting angles for water on certain copolymer films are in the range between 90 and 100°, which is analogous to the values for PDMS films adsorbed on surfactants [286].

It has been established that the wetting effect depends strongly on the copolymer concentration, the polysiloxane content, and the length of the blocks. After the removal of the films from the surface of glass, the wettability of the latter resembled that of the homopolymer. Consequently the copolymer is absorbed on the glass–polymer interface during the casting process and remains on the surface after the removal of the film. This is confirmed by the finding that a copolymer film with a high polysiloxane content can be removed from the glass by heating or by treatment with a solvent.

For a comparative analysis, one should bear in mind the study [287] of monomolecular films of polymethyl(n-alkyl)siloxanes on organic liquids, including propylene carbonate.

(b) The properties of SCPC based on organosilicon bischlorocarbonates. SCPC in which the silicon atoms are combined exclusively with carbon apart from being involved in SiOSi linkages have been obtained by interfacial condensation at the boundaries between phases based on the organosilicon diols (XIIIa), (XIIIb), (XIIId), (XXVIIa), and (XXXVIIc) and the bisphenols (XVIIIb), (XVIIIc), and (XXXVIIb) with partial or complete replacement of $COCl_2$ by the corresponding bischlorocarbonates (XIVa), (XIVb), (XIVd), (XXXVIIIa), (XXXVIIIb), (XXXVIIIc), (XIXb), and (XIXc). [31,96,116,164,201,206,207,209,210,288,289] 1,1-Bis-(4-hydroxyphenyl)cyclohexane (BHPC) [31,96,288] and BPA [164,201,289] were used as the aromatic dihydroxy-compounds (DHC).

A characteristic property of the SCPC obtained from BHPC and the bischlorocarbonates (XIVa), (XIVd), (XIXb), and (XIXd) in a mixture with $COCl_2$ is a tendency towards a decrease of the intrinsic viscosity, the softening temperature, and the yield with increasing mole fraction of the bischlorocarbonate in the initial mixture of acid chlorides.

Turbidimetric titration data indicate the formation of copolymers with a fairly narrow molecular weight distribution. X-Ray diffraction analysis of the copolymers [31] reveals a low degree of order in their structure regardless of the nature of the bischlorocarbonate employed, which has been explained by the steric effect of the cyclohexyl group of BHPC, which prevents the crystallisation of the macromolecules.

Thermomechanical curves [31] show that the introduction of ≡Si–O–Si≡ groups into the macromolecule of a BHPC-based homopolycarbonate causes a monotonic decrease of t_g and t_{flow}, which confirms the determinations of t_{soft} in a capillary. A characteristic feature of these curves is the presence of small regions corresponding to the viscoelastic state.

Data for the thermo-oxidative degradation (thermogravimetric analytical method) [31] of copolymers based on BHPC and the bischlorocarbonate (XIVa) show that both the initial rate of gas evolution and the total amount of gaseous products increase. Methane, ethylene, etc. were detected in the decomposition products, which indicates the elimination of the $Si-CH_3$ groups together with CO, CO_2, etc., whose liberation is associated with the degradation of the –OC(O)O– groups.

The amount of water absorbed by the film (E, %) [31] decreases from 0.2% for homopolycarbonate obtained from BHPC to 0.01% for the copolymer based on the bischlorocarbonates (XIVa) and (XIVb), while for the bischlorocarbonates (XIXa) and (XIXb) it is in general close to zero. Furthermore, the copolymers exhibit a higher resistance to the action of aqueous alkali compared to organic polycarbonates. Among the series of specimens investigated, the copolymers with 30% of organosilicon fragments showed the greatest resistance to hydrolysis [31]. An important property of the copolymers obtained is their effective adhesion to glass [31].

Protective films made of the copolymers deposited on silicate glass by immersion in 3–5% solutions in chloroform do not impair the optical properties of the glass but at the same time increase its resistance to impact and wear by erosion under dynamic conditions.

The study of the dielectric characteristics of the copolymer based on BHPC and its analogues modified with the bischlorocarbonates (XIVa) and (XIVb) showed [31] that the volume resistivities ρ_V of both copolymers are in the range $(3.0-4.0) \times 10^{15}$ Ω cm; when the frequency increases from 100 to 1×10^6 Hz, tanδ for SCPC modified by the bischlorocarbonate (XIVa) rises from 4×10^{-3} to 9.7×10^{-3}, while that of the specimen modified with the bischlorocarbonate (XIVb) rises from 2.7×10^{-3} to 7.6×10^{-3}. The dielectric constant remains virtually unchanged (2.3) in the same frequency range. At 50 Hz, the dielectric strengths of the copolymers are 300 and 210 kV mm^{-1} respectively for the SCPC incorporating the $O[SiMe_2CH_2-]_2$ and $O[SiMe_2CH_2OCH_2CH_2-]_2$ groups.

The copolymers are formed in the form of viscous transparent liquids (which can be drawn into filaments), waxy masses, or colourless powders soluble in benzene, toluene, chlorohydrocarbons, etc. Depending on the method of synthesis and the type and ratio of the organic and organosilicon components of the initial mixture, the softening temperature varies from 25° to 175°C and is lower the greater the number of siloxy-units in the copolymer. The copolymers are resistant to hydrolysis.

The transparency of films 40–50 μm thick, cast from solution, to light in the visible region reaches 80–85%. An increase of transparency with increasing content of siloxane groups has been noted.

It is noteworthy that both elastic [31] and brittle [164] SCPC have been obtained from the bischlorocarbonate (XIVa). Elastic and at the same time strong films have been made from bischlorocarbonates with a higher silicon content.

Furthermore, in contrast to the SCPC with $\equiv SiOC_{Ar}$ fragments where an increase of the number of ≡Si–O linkages leads to a decrease of thermal stability [173], the copolymers based on organosilicon bischlorocarbonates containing carbofunctional substituents lose weight starting from 300°C and decompose vigorously at 400–450°C.

Consequently, the introduction of siloxane-containing fragments into the macromolecules of rigid-chain polycarbonates increases to some extent the elasticity of the copolymer and reduces t_{soft} and t_{flow}, which is of great practical importance, when the thermal stability is maintained, since it simplifies the conditions necessary for the processing of the polycarbonates by casting under pressure. The capacity of the copolymer for adhesion combined with effective optical characteristics, impact strength, and erosion resistance suggests that they may prove to be valuable constructional materials. The decrease of the amount of water absorbed by the films due to the hydrophobic organosilicon components can probably be used to reduce the hygroscopicity of the polycarbonate when it is stored in granular or powder form.

V. PRACTICAL APPLICATIONS OF SILICON-CONTAINING POLYCARBONATES AND RELATED COMPOUNDS

By virtue of the successful combination of the practically useful properties characteristics of polysiloxanes and polycarbonates, the SCPC and related compounds, mixtures, and compositions may find and are already finding extensive applications in various branches of science and engineering.

Silicon-containing polycarbonate resins possess effective mechanical [31,96,138,143,164,170,175,176,179,181–185,188,194,196,197,201–204,220,221,285,290,291,294], optical [31,64,96,170,172,175,181,182,201,206,210,216,288,292], and dielectric [31,96,164,168,172,221] properties, exhibit thermal stability and resistance to thermal oxidation [10,11,31,96,164,168,172–174,179,180,184,185,199,204,218,220,261,294,295], are fire- [204,262,295] dirt-, oil-, petrol-, and water-resistant [31,96,257,263], etc. which, considered as a whole, makes it possible to regard them as a new independent group of silicone materials [6,12,26,27,96,142,144,150,164,169,170,173–177,181–185,187,188,190,191,195,205,210,218,220,221,223,226,246,255,256,291,294,296].

The SCPC specimens investigated have molecular weights up to 150 000 [96,164,175,196,199,201] and can be readily converted into fibres, films, and other articles. For example, the film-forming properties of the SCPC [31,144,164,168,176,177,180–185,188,192,193,197–200,206,207,216,220,221,297] are used nowadays to obtain protective coatings on wood, paper, metals, glass, textiles, plastics, etc. [31,96,142,164,184,185,188,216,218,230,254,298–301], which can be soft or hard depending on the type and composition of the polymer [31,204,292,293], may be resistant to light and chemical and thermal effects, and may exhibit viscoelastic properties. Even in a thin layer, they are distinguished by impact strength [31,96,138,143,204,292–294], resistance to erosion [31,96], capacity for adhesion to the support [31,96,172,188,225,228], and a unique gas separating capacity [9,31,302–318]. The Dupont and Owens Companies (USA) developed new coatings of the "Glas resins", "Absite", "Sierracin 311", and "Sierracin 900" types, which serve to protect the glass in aeroplane navigation lights, the coating being resistant to scratching

and friction and the action of solvents, fuels, and sea-water [299,300]. Non-misting coatings with satisfactory adhesion to glass and a high transparency [319], hardness, thermal stability, resistance to the action of acetone and dirt [259,263], and capacity to increase the resistance of glass to the frontal pressure of a shock wave [301] are known.

SCPC are used as foam stabilisers in the manufacture of foam polyurethanes [139,217,219,228,229,231], in the manufacture of electrical insulators, dielectric solutions for condensers (KUS 13°), etc. [168,169,177,320], as finishing compositions for sewing thread [321], packing materials, varnishes, binders, hermetically sealing compounds, moulding materials, cements [165,168,177,215,230,233,255-257,322], hair-treatment agents [222], and water-repellent filamental additives to granulated polycarbonates [248]. By virtue of the combination of transparency, softness, wettability, and permeability to oxygen, SCPC are used as materials for optical lenses correcting astigmatism [292].

The presence of silicon in SCPC in a chemically bound form or as an additive to the polycarbonate facilitates the conditions required for their processing, since it lowers the softening temperature and the viscosity, increases the thermal stability, homogeneity, transparency, and moisture resistance, improves the fibre-forming properties, imparts to the material the capacity for internal plasticisation and self-quenching properties, and stabilises the fundamental technical operational characteristics with respect to time [170,171,212-214,235,243-247,261,262,265-267,275,295,323]. Ammonium, substituted ammonium, guanidinium, and alkaline earth metal carbonates facilitates the hardening of polyorganosiloxanes and at the same time play the role of fillers [178,219,229,236,250,251,268-276,278,324]. There is then a possibility of the formation of low-modulus specimens of silicone rubber and of elastic polymeric materials with a low contraction coefficient, improved thermal stability, and adhesion, and other useful properties [276]. Silicon oxides mixed with aluminium and magnesium oxides or separately, silicon carbide, fibreglass, and alkali metal chlorides and bromides are introduced into polycarbonate compositions to promote structure formation, for their reinforcement, to make them fire-resistant, etc. [10,11,142,235,242,258-261,295,325]. Organic and organosilicon percarbonates are used as initiators of the polymerisation of PDMS and their copolymerisation with other monomers, for example styrene and acrylonitrile [165,166,237-240]. After structure formation and hardening, SCPC can be used as moulded articles [218,224,251,252]. The main practical application of SCPC, which has led to a vigorous search for ways of synthesising these polymers and to a comprehensive investigation of their properties, is for the separation of mixtures of gases and vapours. The employment of the gas-separating capacity of SCPC in medicine has been considered in a review [312]. It remains to add that, according to the advertising leaflets of the General Electric Company (USA), the films and capillaries made of block copolymers based on polysiloxanes and polycarbonates of type "MEM-213" combine permeability to gases close to that of the most permeable silicone rubbers [326-347] with a high gas-separating selectivity, which led to the inclusion of these copolymers among the 100 most important industrial products in 1969. [311] They proved to be suitable for use not only in medicine but also in space, under water, etc. [305-310] It has been shown that, when nitriles, vinyl monomers, or aromatic hydrocarbons are deposited by the plasma method on these copolymers in the form of ultrathin coatings with a thickness ≤ 0.5 μm, the ratio of the permeabilities to H_2 and CH_4 increase appreciably (from 0.87 to 33 for PhCN). [305]

A method has been developed for the preparation of ultrathin gas-permeable membranes with a thickness of ~1 μm. [303] It is known that "MEM-213" can form part of more complex polymeric compositions for the same purpose [353]. On the other hand, the search for improved copolymers has continued using other dihydroxy-compounds, including silicon-containing ones [186]. It has been shown that polysiloxanes mixed with hydrated polycarbonates are suitable for the removal of carcinogenic polycyclic hydrocarbons from tobacco smoke [302].

During the preparation of the manuscript for the press, additional studies on the subject of this review were published [354-425].

There are new examples of the synthesis of SCPC [355-358,368-374,405,406,421-423,425] and methods have been described for the preparation of a wide variety of compositions with various properties [373-387,389,399,401,402,413,418-424].

The structure of SCPC has been investigated by X-ray diffraction [360,417], light absorption, light scattering in the presence of various types of deformations [360], and ^1H NMR. [362] Studies have also been made on the chemical, physicomechanical, and dielectric properties of SCPC, the phenomena at interfaces [358,359,361,364,367,388,400,407,410,413,415], and permeability to gases [354,366,412,416].

SCPC have been used in articles required for membrane techniques [354,363,366,407-409,411,412] in electrophotography [389], in medicine in the oxygenation of blood, and in astronautics and aquonautics [354,363,365]. Data have been published on the preparation of SCPC-based film coatings on articles [367,398]; SCPC have also been used to prevent the dyeing of polycarbonates [373] and to stick together the components of various materials [388,396-399,410].

It has been shown that BPA-based polycarbonates are adsorbed from solutions on aerosil [394] and that alkali metal carbonates can serve as fillers for polysiloxanes and as catalysts of their hardening [387], while Ph_3SiCl and Me_3SiCl have been recommended for the regulation of the molecular weights and thermal stabilisation of polycarbonates [424]. Oligomeric bischlorocarbonates have been used in the synthesis of silicon-containing polyurethanes [403,404]. The practical properties of SCPC have been examined in detail in a review [426].

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