The Preparation, Characterization, and Thermal Decomposition Products of Di-Tertiary Butyl-Carbonate and Tertiary Butyl-Chlorocarbonate.

James Wesley Rogers
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THE PREPARATION, CHARACTERIZATION, AND THERMAL DECOMPOSITION PRODUCTS OF DI-TERTIARY BUTYL CARBONATE AND TERTIARY BUTYL CHLOROCARBONATE

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Chemistry

by

James Wesley Rogers
B.A., Hendrix College, 1940
M.S., Louisiana State University, 1942
August, 1947
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ABSTRACT

Dialkyl carbonates and alkyl chlorocarbonates have been well known compounds for a number of years, but members of these two series which have tertiary alkyl groups have apparently been difficult to prepare. This investigation was concerned with the preparation of compounds of this type.

The first example of a carbonate with two aliphatic tertiary alkyl groups is di-tertiary butyl carbonate, the preparation of which is reported here. The first chlorocarbonate with an aliphatic tertiary alkyl group to be isolated and characterized is tertiary butyl chlorocarbonate, the preparation of which is also reported.

Di-tertiary butyl carbonate was prepared by the reaction of gaseous phosgene with a suspension of sodium tertiary butylate in dioxane. This compound melts at 39.5° to 40.5°C. and boils at 158.0°C., at 767.2 mm. pressure. It is an extremely unreactive, stable ester. It is not decomposed at temperatures under 185°C., may be saponified only with difficulty, and does not react with ammonia or phenyl hydrazine.

Tertiary butyl chlorocarbonate was prepared by the reaction of sodium tertiary butylate with a
solution of phosgene in n-butane at -60°C. The reaction was also conducted in three other solvents, and a variety of methods of purification were investigated. The most successful method of purification consisted of low temperature vacuum distillation and treatment with thionyl chloride and liquid bromine. This treatment was necessary to remove tertiary butyl alcohol and an unsaturated compound formed at some time during the preparation. Tertiary butyl chlorocarbonate is hydrolyzed with extreme ease, and begins to decompose thermally at about 100°C.

Quantitative analysis of the gaseous products of the decomposition of tertiary butyl chlorocarbonate indicates that one mole each of carbon dioxide, hydrogen chloride, and isobutylene are produced by each mole of chlorocarbonate that decomposes. No evidence of the existence of any other decomposition product was found.

The kinetics of the decomposition of ethyl chlorocarbonate and isopropyl chlorocarbonate have been studied in these laboratories. The decomposition of these compounds may be represented as follows:

\[ \text{CH}_3\text{CH}_2\text{OCOCl} \rightarrow \text{CH}_3\text{CH}_2\text{Cl} + \text{CO}_2 \]

\[ (\text{CH}_3)_2\text{CHOCOCl} \rightarrow (\text{CH}_3)_2\text{CHCl} + \text{CO}_2 \]

\[ \text{CH}_3\text{CH}==\text{CH}_2 + \text{HCl} + \text{CO}_2 \]

To account for the decomposition, mechanisms have been proposed in terms of the configuration of the activated
complexes. In these theories it is assumed that for decomposition to occur, the chlorine atom must approach the alkyl group. If the chlorine atom can closely approach the alpha carbon atom, a configuration of the activated complex will occur which will result in decomposition into an alkyl halide and carbon dioxide. Since this is the only type of complex which can be formed in ethyl chlorocarbonate, decomposition occurs only in this way. If the chlorine atom approaches the alkyl group from such a direction that it occupies a position between two methyl groups, it will not be near enough to the alpha carbon atom to form the alkyl halide, but will remove a hydrogen atom from the alkyl group to form hydrogen chloride. This results in a rearrangement in the rest of the molecule to produce an unsaturated compound and carbon dioxide. Since isopropyl chlorocarbonate can assume both the above mentioned configurations, it decomposes in both ways.

Present indications are that the decomposition of tertiary butyl chlorocarbonate is in accord with this theory. In a tertiary butyl group, the alpha carbon atom is completely surrounded by three methyl groups, so that, as the chlorine atom approaches the alkyl group, the only possible configuration it can assume is the one in which the chlorine lies between two methyl groups. According to this theory, decomposition must
result in only isobutylene, hydrogen chloride, and carbon dioxide. Analysis of the decomposition products indicates that the theory is correct. Final proof will lie in a complete kinetic study of the decomposition of tertiary butyl chlorocarbonate.
INTRODUCTION

Carbonates and chlorocarbonates with primary and secondary alkyl groups have been well known compounds for a number of years. However, analogous compounds with tertiary alkyl groups have heretofore been elusive. No example has been found in the literature of a carbonate with two tertiary aliphatic alkyl groups. The preparation of tertiary amyl chlorocarbonate has been reported by Merck (56). No attempt was made to isolate the product, and it was identified only by derivatives. The attempted preparation of triphenyl methyl chlorocarbonate has been reported by Bowden (8); but again the compound was not isolated and the only evidence for its existence consists of the identification of decomposition products.

Di-tertiary butyl ether has been prepared by Erickson and Ashton (30) from tertiary butyl chloride and silver carbonate. They were unable to establish that the ether was formed via the decomposition of the carbonate. Investigations of the stability of di-tertiary butyl carbonate would be of interest in connection with this work. It has been shown by Bowden (8) that successive substitution of phenyl groups for hydrogens in dimethyl carbonate induce progressive instability in the
resulting molecules. It might be suspected then, that di-tertiary butyl carbonate is highly unstable.

Extensive work has been done in these laboratories on properties of various chlorocarbonates. The kinetics of the decomposition of ethyl chlorocarbonate has been studied by Choppin, Frediani, and Kirby (18)(19)(32)(47). The kinetics of the decomposition of isopropyl chlorocarbonate has been studied by Compere (21).

Smith (71) has determined the near ultra violet absorption spectra of ethyl, isopropyl, benzyl, and phenyl chlorocarbonates. Dipole moment studies of several chlorocarbonates have been conducted by Wood (77).

Alpha-phenyl ethyl chlorocarbonate has been prepared and characterized by Rogers (67). The thermal decomposition products of this compound were identified.

Differences in the mechanisms of the decompositions of ethyl and isopropyl chlorocarbonates have been found. The ethyl compound decomposes according to the reaction,

\[ C_2H_5OCOCl \rightarrow C_2H_5Cl + CO_2 \]

while the isopropyl compound decomposes in two ways:

\[ (CH_3)_2CHOCOCl \rightarrow (CH_3)_2CHCl + CO_2 \]
\[ (CH_3)_2CHOCOCl \rightarrow CH_3CH=CH_2 + HCl + CO_2 \]

Mechanisms have been proposed by Compere (21) to account for these reactions in terms of the configuration of the activated complexes. The decomposition products obtained from alpha-phenyl ethyl chlorocarbonate indicate
that it decomposes in a manner consistent with these mechanisms. Its decomposition may be represented by two reactions:

\[
\begin{align*}
\text{C}_6\text{H}_5\text{Cl} & \xrightarrow{\text{CHO}} \text{C}_6\text{H}_5\text{CHCH}_3 + \text{CO}_2 \\
\text{C}_6\text{H}_5\text{Cl} & \xrightarrow{\text{CHO}} \text{C}_6\text{H}_5\text{CH=CH}_2 + \text{CO}_2 + \text{HCl}
\end{align*}
\]

It is apparent that studies of the decomposition of tertiary butyl chlorocarbonate will be of great value in proving the proposed mechanisms. The purpose of the present work was to prepare, characterize, and investigate the thermal decomposition of di-tertiary butyl carbonate and tertiary butyl chlorocarbonate.
Preparation of Dialkyl Carbonates

Dialkyl carbonates have been prepared by several different reactions. In most cases, a derivative of carbonic acid is allowed to react with an alcohol or a derivative of an alcohol. Certain simple dialkyl carbonates have been prepared by the decomposition of compounds closely related to the carbonate. While direct esterification of carbonic acid or of its anhydride, carbon dioxide, may be applied to the preparation of monoalkyl carbonates (31), no example has been found of its application to the preparation of a dialkyl carbonate.

Silver carbonate will react with simple aliphatic alkyl halides to produce the dialkyl carbonate. This method is applicable only to the production of those carbonates in which both the alkyl groups are the same. Clermont (20) obtained diethyl carbonate by this reaction. Lieben and Rossi (53) applied it to the production of dibutyl carbonate while Hurtz (78) used it to prepare diisobutyl carbonate.

Gomberg (70) obtained bis(triphenylmethyl) carbonate by the reaction of triphenylmethyl chloride and
silver carbonate.

Potassium ethyl carbonate was alkylated with ethyl sulfuric acid by Chancel (17) to produce diethyl carbonate. Since this reaction requires the preliminary preparation of an alkali metal salt of a monoalkyl carbonate, it apparently has not been further utilized.

Diakyl oxalates may be decomposed to yield the corresponding diakyl carbonates. To prepare diethyl carbonate, Löwig and Weidmann (54) treated diethyl oxalate with sodium or potassium metal. Geuther (34) and Cranston and Dittmar (24) obtained the same compound by treating diethyl oxalate with sodium or potassium. Cahours (11) prepared dipropyl carbonate by the same reaction.

Simple diakyl carbonates are subject to alkyl interchange with higher alcohols in the presence of ethyl magnesium bromide. Frank and co-workers (31) prepared di-secondary butyl carbonate, ethyl cyclohexyl carbonate, and dicyclohexyl carbonate by this reaction.

Phosgene, the acid chloride of carbonic acid, will react with alcohols in the presence of an acid binding agent such as a tertiary amine to produce a carbonate in which both alkyl groups are the same. Bayer and Company (5) obtained a number of such carbonates by treating secondary alcohols with phosgene in the presence of pyridine.

The most versatile method for the preparation of
dialkyl carbonates involves the reaction of a chloro-
carbonate and an alcohol. By this method it is possible
to prepare mixed carbonates in which the two alkyl
groups are different. Röse (68) obtained a number of
such mixed carbonates in which the alkyl groups were
methyl, ethyl, propyl, isobutyl, and isoamyl. Bayer
and Company (6) applied this method to the preparation
of a number of mixed carbonates in which one alkyl
group was methyl or ethyl and the other was from a com-
plex secondary alcohol. Bayer and Company (5) also
found the method applicable to the preparation of high
boiling dialkyl carbonates in which both alkyl groups
are from complex secondary alcohols. Chattaway and
Saerens (16) obtained butyl methyl, butyl ethyl, and
butyl propyl carbonates by the reaction of butyl chloro-
carbonate with methyl, ethyl, and propyl alcohol.
Pawlewski (61) found it helpful to use aluminum chloride
as a catalyst in the preparation of ethyl propyl carbon-
ate from ethyl chlorocarbonate and propyl alcohol.

In those cases in which the reaction of an alcohol
with phosgene or a chlorocarbonate is too sluggish, the
use of the sodium or potassium alcoholate has been found
to be effective. The method has also been applied to
preparations of simple carbonates which may be prepared
by the direct action of the alcohol itself on a chloro-
carbonate. Schreiner (69) prepared dimethyl carbonate
by allowing sodium methyleate to react with methyl
chlorocarbonate. Röse (68) obtained dipropyl carbonate from sodium propylate and propyl chlorocarbonate. His yields, however, were not as good as those obtained by use of propyl alcohol and propyl carbonate. Ethyl isopropyl carbonate was prepared from ethyl chlorocarbonate and sodium isopropylate by Taylor (73). Bowden and Butler (9) found that the introduction of a suspension of sodium hexylate to a phosgene solution yielded dihexyl carbonate. Palomaa, Salmi, and Suoja (60) prepared ethyl tertiary butyl and normal propyl tertiary butyl carbonate by the reaction of sodium tertiary butylate with the corresponding chlorocarbonate. They prepared the sodium tertiary butylate by allowing the alcohol to react with sodamide in ether solution. Diaryl carbonates have been prepared by passing phosgene gas into an alkaline solution of the corresponding phenol. Pearson and Tryon (62) obtained diphenyl carbonate by this procedure. Demmelmeier and von Walther (26) applied this process to the production of diaryl carbonates in which the aryl groups were halogen substituted cresyl groups. They also prepared mixed carbonates by treating methyl or ethyl chlorocarbonate with halogen substituted cresols.

A series of phenylated dimethyl carbonates was prepared by Bowden (8) by the reaction of the corresponding potassium alcoholate with phosgene in a benzene or toluene solution. He prepared carbonates in which the alkyl
groups were benzyl, benzohydryl, and triphenyl methyl.

Counselor (83) found that methyl chlorocarbonate will decompose to yield dimethyl carbonate when treated with lead oxide. Bowden (8) found that phenyl chlorocarbonate decomposes when heated to give diphenyl carbonate and phosgene. The decomposition of the chlorocarbonate does not seem to offer a general method for the preparation of carbonates, however, and has not been further used.

**Stability of Dialkyl Carbonates**

Kitchie (66) investigated the products of pyrolysis of dialkyl carbonates. He concluded that if the alkyl groups are such that an olefin can be formed, the products will be the olefin, carbon dioxide, and an alcohol. For mixed carbonates in which two olefins can be formed, the reaction proceeds by both paths. In those cases where no olefin can be formed from the alkyl group, pyrolysis products are carbon dioxide and an ether. The esters, products, and pyrolysis temperatures are as follows:

<table>
<thead>
<tr>
<th>Ester</th>
<th>Temperature</th>
<th>Pyrolysis products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl carbonate</td>
<td>500°-600°C.</td>
<td>methyl alcohol, ethylene, carbon dioxide, carbon monoxide, and hydrogen</td>
</tr>
<tr>
<td>Diethyl carbonate</td>
<td>500°C.</td>
<td>ethyl alcohol, ethylene, carbon dioxide</td>
</tr>
</tbody>
</table>
Ester Pyrolysis products

<table>
<thead>
<tr>
<th>Ester</th>
<th>Temperature</th>
<th>Pyrolysis products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl butyl carbonate 500°C.</td>
<td>Ethyl alcohol, butylene, carbon dioxide</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Butyl alcohol, ethylene, carbon dioxide</td>
</tr>
<tr>
<td>Diphenyl carbonate 640°-70°C.</td>
<td>Diphenyl ether, carbon dioxide</td>
<td></td>
</tr>
<tr>
<td>Phenyl ethyl carbonate 500°C.</td>
<td>Phenol, ethylene, carbon dioxide</td>
<td></td>
</tr>
</tbody>
</table>

Bowden (8) investigated the decomposition temperatures of the series of phenylated dimethyl carbonates whose preparation has been described previously. He found that successive substitution of phenyl groups for hydrogen atoms in dimethyl carbonate resulted in progressive instability in the resulting molecule. He describes the decomposition temperatures of this series as follows:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Decomposition Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl Carbonate</td>
<td>500°C.</td>
</tr>
<tr>
<td>Dibenzyl Carbonate</td>
<td>350°C.</td>
</tr>
<tr>
<td>Dibenzohydryl Carbonate</td>
<td>260°C.</td>
</tr>
<tr>
<td>Bis (triphenylmethyl) Carbonate</td>
<td>208°C.</td>
</tr>
</tbody>
</table>

Erickson and Ashton (30) have pointed out the possibility that di-tertiary butyl carbonate may be unstable. They prepared di-tertiary butyl ether by the reaction of silver carbonate and tertiary butyl chloride but were unable to establish that the ether was formed.
via the decomposition of the carbonate.

Preparation of Alkyl Chlorocarbonates

Chlorocarbonates may be prepared by the action of phosgene on an alcohol. Although the fundamental reaction is the same in practically all cases, a great many variations in the methods of procedure have been utilized in efforts to obtain better yields. Certain chlorocarbonates may be prepared by the chlorination of the corresponding formates; this reaction has not received a great deal of attention, however, since the formates themselves are difficult to prepare and the conditions and the extent of chlorination are difficult to control.

Several workers have prepared various chlorocarbonates by adding the corresponding alcohol to liquid phosgene. Hesse (68) prepared methyl, ethyl, propyl, isobutyl, and isoamyl chlorocarbonates by adding the proper alcohol to liquid phosgene in the presence of sunlight. Hentschel (40) prepared methyl chlorocarbonate by the same method but did not find it necessary to conduct the reaction in the presence of sunlight. Thiele and Dent (74) prepared benzyl chlorocarbonate from benzyl alcohol and liquid phosgene at -8°C. Spica and DeVarda (72) applied this method to the preparation of isopropyl chlorocarbonate. Chloroalkyl chlorocarbonates have been prepared by this method by several workers (1)(2)(12)(15)(38)(63)(70). In some cases,
complex alcohols will react with liquid phosgene to produce chlorocarbonates (3)(14)(45)(55).

Frequently, the reaction between phosgene and an alcohol will proceed more smoothly if the phosgene is dissolved in a solvent. Bergmann and Zervas (7) made benzyl chlorocarbonate by allowing benzyl alcohol to react with a toluene solution of phosgene. Dox and Yoder (29) prepared gamma-chloropropyl chlorocarbonate by the same procedure. Chattaway and Saerens (16) obtained butyl chlorocarbonate by dissolving phosgene in a large excess of butyl alcohol and fractionating rapidly. This method gave low yields of the chlorocarbonate because if the fractionation was not extremely rapid, the excess alcohol reacted with the chlorocarbonate to produce dibutyl carbonate.

Capelli (13) added methyl or ethyl alcohol to phosgene absorbed on charcoal to produce the corresponding chlorocarbonates.

The reaction between a number of alcohols and phosgene has been found to be greatly facilitated by the presence of an agent which will remove hydrogen chloride. Several tertiary amines have been used as the acid binding agent, but conflicting reports of the effectiveness of various amines have been presented. Hofmann (43) prepared chlorocarbonates by the reaction of a solution of phosgene in an inert organic solvent with a mixture of the corresponding alcohol and a tertiary amine such as
quinoline, antipyrine, or dialkyl aniline. He reports that the use of pyridine as an acid binding agent results in the formation of the dialkyl carbonate. Bayer and Company (4)(5) prepared ethyl, benzyl, and phenyl chlorocarbonates by allowing the corresponding alcohol to react with phosgene dissolved in benzene in the presence of antipyrine, quinoline, and dimethyl aniline. They found that pyridine is unsuitable as an acid binding agent in these preparations. However, Lirscherl (27) succeeded in the preparation of the chlorocarbonate of a complex alcohol using pyridine as an acid binding agent. Rogers (67) prepared alpha-phenyl ethyl chlorocarbonate using pyridine as an acid binding agent but reported unsuccessful attempts to prepare the same chlorocarbonate when dimethyl aniline was used similarly. Merck (56)(57), Kenyon, Phillips, and Pittman (46), and Raiford and Inman (64) reported similar preparations using a variety of alcohol solvents and acid binding tertiary amines. Oesper, Broker, and Cook (59) applied this method with two variations. In the first variation, they dissolved phosgene in tertiary amines and added the alcohol slowly. In the second variation, phosgene was dissolved in the alcohol and the tertiary amine added slowly.

Chlorocarbonates may be prepared from sodium or potassium alcoholates and phosgene. This method eliminates the necessity of an acid binding agent since an
alkali metal chloride is split out instead of hydrogen chloride. Hochstetter (41) prepared aromatic chlorocarbonates from two-phase systems by dissolving phenols in aqueous alkali and adding a solution of phosgene in a solvent immiscible with water. Bowden (8) prepared benzohydryl chlorocarbonate from the potassium alcoholate and phosgene in a non-aqueous medium. He reported unsuccessful attempts to prepare triphenyl methyl chlorocarbonate by the same procedure. Copisarov (22) made p-cresyl chlorocarbonate from p-cresol in sodium hydroxide solution and phosgene. Freudenberg and co-workers (33) Nekrasov and Komisarov (58), and Hoeflake (42) have reported similar preparations.

Methyl and substituted chloromethyl chlorocarbonates may be prepared by the chlorination of methyl formate in the presence of light. It is difficult to control the extent of chlorination, and a mixture of the various chlorinated methyl carbonates is obtained. Kling and co-workers (48)(49)(50) prepared methyl chlorocarbonate by this reaction. Hentschel (40), Grignard and co-workers (36)(37), Criscuoli (25) and Disrens (28) reported the preparation of methyl, monochloromethyl, dichloromethyl, and trichloromethyl chlorocarbonates by this process.

**Decompositions of Alkyl Chlorocarbonates**

Choppin, Frediani, and Kirby (18)(19)(32)(47) reported that ethyl chlorocarbonate decomposes in a
homogeneous unimolecular reaction to give ethyl chloride and carbon dioxide. This compound may be decomposed catalytically with zinc chloride (76) or aluminum chloride (47) to give ethylene and hydrogen chloride in addition to the above mentioned products. Compere (21) found that isopropyl chlorocarbonate decomposes thermally according to two mechanisms:

\[
(CH_3)_2CHOCl \longrightarrow (CH_3)_2CHCl + CO_2
\]
\[
(CH_3)_2CHOCl \longrightarrow CH_3CH=CH_2 + HCl + CO_2
\]

Mechanisms have been proposed which account for the decompositions of ethyl and isopropyl chlorocarbonate. Alpha-phenyl ethyl chlorocarbonate (67) decomposes to give alpha-phenyl ethyl chloride, styrene, hydrogen chloride, and carbon dioxide. Apparently this decomposition is analogous to that of isopropyl chlorocarbonate.

\[
(C_6H_5)(CH_3)CHOCl \longrightarrow (C_6H_5)(CH_3)CHCl + CO_2
\]
\[
(C_6H_5)(CH_3)CHOCl \longrightarrow C_6H_5CH=CH_2 + HCl + CO_2
\]

Lessig (52), in investigations of the thermal decomposition of isobutyl chlorocarbonate obtained final pressures of more than twice the initial pressure indicating decomposition into three molecules. Phenyl chlorocarbonate has been found to decompose to diphenyl carbonate and phosgene (8). Trichloromethyl chlorocarbonate may follow two mechanisms in its decomposition.

\[
\text{heat} \quad \text{Cl}_3\text{COCOCl} \xrightarrow{} 2\text{COCl}_2
\]
\[
\text{AlCl}_3 \quad \text{Cl}_3\text{COCOCl} \xrightarrow{} \text{CCl}_4 + \text{CO}_2
\]
The first of these decompositions is obviously impossible for the alkyl chlorocarbonates which have no chlorine substituted in the alkyl group. The second mechanism is analogous to the decomposition of alkyl chlorocarbonates producing alkyl halides.

Thus, various chlorocarbonates have been found to decompose according to three different mechanisms: The first gives an alkyl halide and carbon dioxide, the second gives an unsaturated hydrocarbon, hydrogen chloride, and carbon dioxide, and the third gives a diaryl carbonate and phosgene.
EXPERIMENTAL
DI-TERTIARY BUTYL CARBONATE

Preparation

Di-tertiary butyl carbonate was prepared by allowing phosgene to react with excess sodium tertiary butylate in dioxane solution. Sodium tertiary butylate was prepared by refluxing 60 g. of tertiary butyl alcohol in 600 ml. of dioxane over 17.3 g. of sodium wire until the sodium had reacted completely. This solution was placed in a two-liter, three-necked flask equipped with a stirrer, a dry-ice-cooled bucket condenser, and an inlet tube for phosgene. Thirty-six and nine-tenths grams of liquid phosgene were placed in a 50 ml. flask attached to the inlet tube. The rate of introduction of gaseous phosgene was controlled by cooling or warming the 50 ml. flask. Gaseous phosgene was introduced into the alcoholate suspension, which was maintained at 60° to 85°C. Approximately one and one-fourth hours were required for the reaction to take place. The mixture was stirred for one hour at 65°C., then poured into two liters of ice and water. A crystalline material separated and floated on the water layer. The crystals were filtered off, melted with warm water, and washed in a separatory funnel. After separating the oil layer,
It was filtered through ordinary filter paper into a 50 ml. Claisen flask. The oil was then distilled under vacuum and a fraction collected which boiled from 94.5° to 96.5°C, under 90 mm. to 91 mm. pressure. The product was recrystallized from an ethyl alcohol-water mixture, forming white flaky crystals (melting point, 39.5° to 40.5°C.—uncorrected). These crystals were purified by sublimation, but the melting point was unchanged. The yield of di-tertiary butyl carbonate by this method was 40.5 percent.

Analysis.

The percent carbon and hydrogen in di-tertiary butyl carbonate was determined by semi-micro combustion analysis.

Percent Composition

<table>
<thead>
<tr>
<th>Element</th>
<th>Calculation</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>62.04%</td>
<td>61.88%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>62.58%</td>
</tr>
<tr>
<td></td>
<td>average = 62.23%</td>
<td></td>
</tr>
<tr>
<td>Hydrogen</td>
<td>10.41%</td>
<td>10.64%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.62%</td>
</tr>
<tr>
<td></td>
<td>average = 10.63%</td>
<td></td>
</tr>
</tbody>
</table>

The saponification equivalent of di-tertiary butyl carbonate was determined by heating a weighed sample of the carbonate with 25 ml. of standard 0.25 N potassium hydroxide in triethylene glycol and 25 ml. of 5 percent barium chloride. In order to achieve complete saponification, it was necessary to heat the samples for nine
hours at 170°C. The barium chloride was included in order to remove the carbonate ion as an insoluble precipitate. The excess potassium hydroxide was titrated with standard 0.1 N hydrochloric acid to the methyl orange end-point. The results obtained were as follows:

<table>
<thead>
<tr>
<th>Calculated</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>174.2</td>
<td>174.0</td>
</tr>
<tr>
<td>173.6</td>
<td></td>
</tr>
<tr>
<td>average = 173.8</td>
<td></td>
</tr>
</tbody>
</table>

**Characterization.**

The procedure for the determination of the melting point of di-tertiary butyl carbonate and of the boiling point at 90 mm. to 91 mm. has been described previously. The boiling point at atmospheric pressure was determined as follows: A 1 ml. sample of di-tertiary butyl carbonate was placed in a semi-micro fractionation apparatus which had a one-inch section packed with one-eighth inch, single-turn, glass helices. The carbonate was found to distill at constant temperature.

- Melting point = 39.5° to 40.5°C. (uncorrected)
- Boiling point = 94.5° to 96.5°C. at 90mm. to 91mm.
- Boiling point = 158.0° at 767.2mm.

**Derivatives.**

One-half gram of di-tertiary butyl carbonate, 50 ml. of a tri-ethylene glycol solution of potassium hydroxide, and one gram of barium chloride were mixed and heated under a reflux condenser for two and one-half hours. The flask was then cooled and 10 g. of the mixture was distilled out of the flask. This liquid was treated with calcium
oxide to remove any water present and extracted with benzene several times. The resulting solution was treated with 1.5 g. of phenyl isocyanate. The solution was heated to boiling, and after standing for six hours, was evaporated to a volume of 1 ml. and cooled. The resulting crystals were extracted with petroleum ether (boiling range, 65° to 70°C.) and recrystallized. These crystals were found to be tertiary butyl N-phenyl carbamate (melting point, 136.0° to 136.5°C.) (mixed melting point with an authentic sample of tertiary butyl N-phenyl carbamate, 135.8° to 136.3°C.) (51). This derivative indicates that the alcohol saponification product from the ester was tertiary butyl alcohol.

The precipitated solid from the above saponification was filtered and washed thoroughly with water. The solid was treated with concentrated hydrochloric acid and the evolved gases were bubbled through lime water. A white precipitate of calcium carbonate resulted. This was considered sufficient evidence for the fact that the precipitate was barium carbonate, which would indicate that the ester saponified was an alkyl carbonate.

Attempts were made to prepare derivatives of the carbonate by allowing it to react with ammonia and with phenyl hydrazine. No crystalline product was obtained after heating 0.5 g. of di-tertiary butyl carbonate with 10 ml. of concentrated ammonium hydroxide in a sealed ampule at 150°C. for forty hours. One gram of
di-tertiary butyl carbonate and 2.5 g. of phenylhydra-
azine were heated in a sealed ampule at from 175° to
185°C. for 172 hours. From this mixture, di-tertiary
butyl carbonate was recovered unchanged. This carbonate
is apparently much less reactive than are other dialkyl
carbonates, and it is not decomposed appreciably at
temperatures below 185°C.
Preparation.

All efforts to prepare tertiary butyl chlorocarbonate by the reaction of tertiary butyl alcohol and phosgene were unsuccessful. Attempts were made using these two reactants alone and in the presence of quinoline and of dimethyl aniline. In most cases no reaction of any type was apparent. It therefore seemed necessary to use a more reactive derivative of the alcohol in order to prepare the chlorocarbonate. Sodium tertiary butylate was selected as the most likely compound fulfilling this requirement. The primary reaction used in the preparation may be written as follows:

\[(\text{CH}_3)_3\text{C} \text{Na} + \text{COCl}_2 \rightarrow (\text{CH}_3)_3\text{COCOCl} + \text{NaCl}.\]

The reaction was conducted under a variety of conditions. In practically every case, the chlorocarbonate was obtained; however, its isolation in the pure form proved to be quite difficult.

After the reaction was performed and the product purified, it was analyzed by introducing a weighed sample sealed in a small glass bulb into a glass-stoppered flask containing aqueous ammonia. The bulb was broken by shaking and the flask allowed to stand...
until all of the chlorocarbonate had reacted. The solution was then acidified with 6 N nitric acid, and the chloride was determined by a Volhard titration. Results were expressed as percent chlorocarbonate, assuming all the chloride came from the compound. Conditions under which the reaction was conducted, methods of purification, and the resulting purities are described in the following sections.

Method I. Benzene was used as a solvent in several preparations of tertiary butyl chlorocarbonate. In each case, sodium tertiary butylate was prepared in a benzene solution by allowing sodium wire to react with excess tertiary butyl alcohol in a benzene solution. After all the sodium had reacted, most of the liquid was distilled away in order to remove excess alcohol. Fresh benzene was added and the mixture was refluxed until a uniform suspension of the alcoholate resulted. The reaction between phosgene and sodium tertiary butylate took place in a one-liter, three-necked flask, equipped with a mercury sealed stirrer, an outlet tube, and a steam-jacketed dropping funnel. A solution of phosgene in benzene was prepared in the flask which was cooled in an ice-salt mixture. The suspension of the alcoholate and benzene was introduced slowly from the dropping funnel over a period of from two to five hours. It was necessary to maintain this suspension near the boiling point of benzene in order to prevent the crystallization
of the alcoholate. Immediately after introduction of
the alcoholate, a small sample of the reaction mixture
was added to an ether solution of aniline. The ether
was evaporated, and the products recrystallized from
petroleum ether (boiling range 63° to 70°C.). The
crystals were identified as tertiary butyl N-phenyl
carbonate (melting point, 136° to 137°C.). This deriv-
avative proved the presence of tertiary butyl chlorocar-
bonate in the reaction mixture. In preparations in
which the reaction mixture was washed with ice water
to remove the colloidal sodium chloride, the chlorocar-
bonate was destroyed. Several of the reaction mixtures
were filtered through fritted glass filters in order
to remove the sodium chloride. The colloidal nature of
the precipitate made filtration so slow that quite an
appreciable amount of the product was hydrolyzed before
filtration was completed. Another mixture was filtered
through fritted glass after absorbing the colloidal
sodium chloride on the surface of amorphous silica. This
procedure permitted much faster filtration. In all cases
the benzene was evaporated under vacuum between 0°C. and
20°C. After these treatments no chlorocarbonate was iso-
lated from any of the preparations.

Method II. Preparations of tertiary butyl chloro-
carbonate were conducted in 1,4-dioxane. The method of
procedure was the same as in Method I, except that the
alcoholate was prepared in dioxane solution. The reaction
took place at temperatures from $0^\circ$ to $15^\circ$C. After reaction was complete, the mixture was washed rapidly with ice water to remove sodium chloride, dioxane, and the excess phosgene. In all cases, the chlorocarbonate was completely destroyed by this treatment, but small amounts of di—tertiary butyl carbonate were isolated.

After experiments with the first two methods, it was determined that the chlorocarbonate hydrolyzed so readily that long exposures to the atmosphere would destroy it, and that extensive decomposition would occur at room temperature.

Method III. Preparations of tertiary butyl chlorocarbonate were made with diethyl ether as the solvent. Sodium tertiary butylate was prepared as previously described, but the solvent was distilled away completely, and the resulting product was dried under vacuum on a steam bath and ground to a fine powder. This solid material was then added slowly to an ether solution of phosgene which was cooled with a dry ice-acetone mixture. During the course of the reaction, the temperature was not allowed to rise higher than $-40^\circ$C. in any case. After reaction was complete, the mixture was filtered through fritted glass using amorphous silica as a filter aid. Crystallization following the evaporation of the ether yielded a product which was 51.8 percent chlorocarbonate. Recrystallization from ethyl bromide failed to improve the purity of the compound. Recrystallization from an ether–petroleum ether (boiling range, 33°
to $38^\circ$C. \) mixture yielded a product which was 66.5 percent chlorocarbonate.

Repeated crystallization from the ether-petroleum ether mixture resulted in small improvement in the product. The impurities either crystallized with or were occluded by the chlorocarbonate.

Method IV. The chlorocarbonate was prepared with excess phosgene serving as a solvent. The alcoholate was prepared as described in Method III and added to the liquid phosgene slowly with strong stirring, at temperatures not above $-45^\circ$C. Sodium chloride was removed by filtration through fritted glass, and excess phosgene was removed by evaporation under vacuum at $-20^\circ$C. The product was then distilled as rapidly as possible at 40 mm. Distillation was so slow that the temperature of distillation was not determined. The product thus obtained was 48 percent tertiary butyl chlorocarbonate.

Method V. Ethyl chloride was used as a solvent in certain preparations of the chlorocarbonate. In all cases, the alcoholate was prepared by allowing sodium wire to react with a large excess of tertiary butyl alcohol which was then removed by distillation. The alcoholate was freed from remaining traces of the alcohol by heating several hours on a steam bath under vacuum. The solid alcoholate was then added to an ethyl chloride solution of phosgene at temperatures not higher than $-65^\circ$C.
In the first preparation, sodium chloride was removed by filtration through fritted glass with amorphous silica as a filter aid. Ethyl chloride was evaporated under vacuum and the chlorocarbonate was crystallized from the resulting crude products. These crystals were 63 percent chlorocarbonate.

In the second preparation, sodium chloride was removed by centrifuging. Centrifuge tubes were packed in dry ice and stoppered tightly during centrifuging. As it proved impossible to pack enough dry ice around the tubes to keep them cold during long periods of time in the centrifuge, it was necessary to spin each sample several times to remove the sodium chloride completely. The colloidal precipitate, however, never separated cleanly, and large amounts of the ethyl chloride solutions were lost. Maximum purity obtained by this method was 22 percent.

Method VI. Normal butane was used as the solvent in the succeeding preparations. In all of these preparations, sodium tertiary butylate was added as a dry powder. The alcoholate retained alcohol so tenaciously that from twenty-four to thirty-six hours of heating on a steam bath under vacuum were required to achieve constant weight of the alcoholate. In several preparations, the alcoholate was partially dried in this fashion, then dissolved in boiling benzene, recrystallized, and filtered. The resulting product could be freed from benzene
much more readily than from alcohol, but in all cases, the crystals which were obtained were colored. In the last preparation, the alcoholate was prepared in a large excess of tertiary butyl alcohol which was then cooled to room temperature precipitating the alcoholate. The product was then separated by filtration and dried in the usual fashion. Experiments on the solubility of sodium hydroxide in tertiary butyl alcohol indicated that if any of this compound formed during refluxing, it would remain in the alcohol solution, and consequently would be removed from the desired product. The alcoholate obtained in this fashion was a pure white, light, fluffy powder.

In the course of these preparations, several filter aids were used in attempts to determine the most expeditious method of removing the colloidal sodium chloride. Amorphous silica, "Hyflo Super Cel", crystalline silica, and mixtures of Super Cel and crystalline silica were used. Most rapid filtration was obtained by filtering the reaction mixture through a three-quarter-inch bed of crystalline silica in a vacuum-jacketed fritted glass Füchner funnel. In all of these cases, after removal of the sodium chloride, the butane and excess phosgene were removed by evaporation under vacuum at -20°C. The main impurity present in the chlorocarbonate produced by these preparations was found to be tertiary butyl alcohol. In the first preparations, cooling the butane
solution to −70°C immediately after removal of the sodium chloride resulted in the deposition of crystals. These were filtered off and identified as tertiary butyl alcohol by boiling point and by reaction with phenyl isocyanate to produce tertiary butyl N-phenyl carbamate, (melting point, 136.0° to 137.0°C.). In later preparations, the purity of the alcohohate was improved to the point where no alcohol could be precipitated in this fashion.

Several different methods of treatment of the crude chlorocarbonate were utilized in attempts to prepare the pure samples of the compound. Ordinary vacuum distillation resulted in considerable decomposition of the chlorocarbonate. Therefore, a distillation apparatus was constructed in which the distilling flask and side arm were completely immersed in ice water; and the receiver, placed as close to the flask as possible, was immersed in a dry-ice-acetone mixture. Thus, at no time during the distillation was the product allowed to rise to a temperature higher than 10°C. Distillation temperature was determined by noting the temperature of the water in which the distilling flask was immersed. Distillation proceeded at pressures of the order of 1 mm. of mercury. This method was equivalent to a single plate distillation, and therefore was not suitable alone as a method of purification. Because of the extreme ease with which the chlorocarbonate was hydrolyzed, it was desirable to
reduce to a minimum the number of operations necessary for purification; and for this reason, a chemical method for removing the alcohol seemed advisable. Several attempts were made to remove the alcohol by the use of phosphorus pentoxide both before and after removal of the solvent butane. Since it was necessary to remove the phosphorus pentoxide by filtration, an operation was introduced which exposed the chlorocarbonate to the atmosphere. Products ranging from 81 percent to 97.6 percent chlorocarbonate were obtained by this method. Since the purity varied over a wide range and could not be controlled, the method was not considered practicable.

Several runs were made in which thionyl chloride was used to react with the alcohol. In these preparations, the chlorocarbonate was first distilled and assayed. The theoretical amount of thionyl chloride was calculated with the assumption that all the impurity was tertiary butyl alcohol. This quantity of thionyl chloride was introduced slowly into the crude chlorocarbonate at temperatures below -20°C. The mixture was then subjected to vacuum at -20°C in order to remove the hydrogen chloride and sulfur dioxide which were formed. The product was then redistilled to remove the tertiary butyl chloride formed. The maximum purity obtained by this treatment was 98 percent.

One preparation was attempted in which sulfuryl chloride was used in place of thionyl chloride in an
effort to obtain a product of higher purity. The sulfuryl chloride reacted with the alcohol, liberating hydrogen chloride. Sulfuric acid was formed by this reaction, and separated as a second liquid phase. Before the organic liquid could be removed, some carbonization took place, as evidenced by the darkening of the acid layer. For this reason, the reagent used was not satisfactory. The best product thus obtained was 96 percent chlorocarbonate. Since the impurities cannot be removed by distillation, they must boil close to the chlorocarbonate. If the impurity were not all alcohol, the only reasonable possibility found was that diisobutylene had been formed either by the thionyl chloride reacting with alcohol or by the decomposition of the chlorocarbonate. Experiments with diisobutylene showed that it absorbed bromine readily at $-20^\circ\text{C.}$ and that it was rendered non-volatile under conditions of the chlorocarbonate distillation by this treatment.

On the assumption that diisobutylene was present, liquid bromine was added to a sample of the product which had been treated with thionyl chloride. It was found that, at a temperature of $-20^\circ\text{C.}$, an appreciable quantity of bromine was absorbed by the mixture. Liquid bromine was added until a permanent light yellow color was obtained; excess bromine was removed by evacuation, and the product was distilled. This yielded a product of higher purity than was obtainable by the use of thionyl
chloride alone. In the final preparation, two treatments of thionyl chloride followed by bromine addition and distillation resulted in a product which was 99.3 percent chlorocarbonate. Details of this preparation are as follows:

A solution of 165 g. of phosgene in 200 ml. of liquid butane was prepared and cooled to below -60°C. Ninety-three and five-tenths grams of dry powdered sodium tertiary butylate were added over a period of five hours with strong stirring. The mixture was stirred one-half hour longer and allowed to stand several hours, during which time the sodium chloride partially settled out. The mixture was filtered through a layer of crystalline silica which had been dried in an oven at 130°C. Excess phosgene and butane were evaporated under vacuum at temperatures of -15°C to -30°C. The resulting product was distilled and a fraction was collected which boiled at from 4°C to 16°C, from 1.5 mm. to 8 mm. pressure. This fraction was treated with 8.5 gm. of thionyl chloride at -70°C, then placed under vacuum for two hours at -20°C. Liquid bromine was added drop-wise until a faint yellow color persisted. The liquid was again distilled, and a fraction collected which boiled at 3°C to 6°C, at 1 mm. to 3.5 mm. pressure. This liquid was treated with 3 g. of thionyl chloride and with liquid bromine as before. Distillation yielded a product which boiled at 3°C to 4°C, and at 0.9 mm. to 1.7 mm.
pressure. Analysis showed this product to be 99.3 percent chlorocarbonate. Subsequent distillation did not change the purity. The yield of tertiary butyl chlorocarbonate was 20.4 percent.

A summary of the data on the preparation of tertiary butyl chlorocarbonate is presented in the appendix. In all preparations, the solvent was evaporated under vacuum prior to the purification of the product listed in the table.

Analysis.

The percent chlorine in tertiary butyl chlorocarbonate was determined gravimetrically. A weighed sample was introduced into a flask containing dilute ammonium hydroxide. After the reaction was complete, the solution was acidified; excess silver nitrate was added, and the precipitated silver chloride was filtered, dried, and weighed. The percent carbon and hydrogen in the compound were determined by semi-micro combustion analysis.

Percentage Composition

<table>
<thead>
<tr>
<th>Element</th>
<th>Calculated</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine</td>
<td>25.96%</td>
<td>25.78%</td>
</tr>
<tr>
<td></td>
<td>25.79%</td>
<td>25.80%</td>
</tr>
<tr>
<td></td>
<td>average = 25.79%</td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>43.97%</td>
<td>43.8%</td>
</tr>
<tr>
<td></td>
<td>43.6%</td>
<td>43.7%</td>
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<tr>
<td></td>
<td>average = 43.7%</td>
<td></td>
</tr>
<tr>
<td>Hydrogen</td>
<td>6.64%</td>
<td>6.88%</td>
</tr>
<tr>
<td></td>
<td>6.84%</td>
<td>6.86%</td>
</tr>
<tr>
<td></td>
<td>average = 6.86%</td>
<td></td>
</tr>
</tbody>
</table>
Derivatives.

1. Tertiary butyl N-phenyl carbamate.

To one g. of aniline and 40 cc. of cold ethyl ether, one g. of tertiary butyl chlorocarbonate was added. After the mixture had stood in an ice bath for fifteen minutes, 30 ml. of distilled water were added forming a two-phase system. The ether was evaporated with a heat lamp and a stream of dry air. When most of the ether had evaporated, the heat lamp was cut off, 2 ml. of 6 N nitric acid were added, and the evaporation of ether was finished slowly with a stream of dry air. The carbamate crystallized and floated on the water. The mixture was filtered and the carbamate crystallized from petroleum ether (boiling range, 63° to 70°C.).

The melting point of tertiary butyl N-phenyl carbamate was 136.3° to 136.5°C. (uncorrected).

The melting point of tertiary butyl N-phenyl carbamate, prepared from tertiary butyl alcohol and phenyl isocyanate (51)(44), was 136.0° to 136.5°C. The mixed melting point of this carbamate and that made from tertiary butyl chlorocarbonate and aniline was 136.2° to 136.5°C. The value reported in the literature is 136.0°C. (51).


This carbamate was prepared from tertiary butyl chlorocarbonate and toluidine by the same procedure as that used for tertiary butyl N-phenyl carbamate. Its
melting point, which was unchanged by crystallization from petroleum ether (boiling range, 63° to 70°C.), was 92.0° to 93.0°C. (uncorrected). This compound has not been previously reported in the literature.

**Thermal Decomposition Products.**

Qualitative analysis of the decomposition products of tertiary butyl chlorocarbonate demonstrated the presence of carbon dioxide, hydrogen chloride, and an unsaturated hydrocarbon which was assumed to be isobutylene. No evidence of the presence of tertiary butyl chloride was found. For purposes of quantitative determination of the decomposition products, samples of chlorocarbonate were heated in sealed 200 ml. bulbs at 170°C. for thirty-six hours. To determine hydrogen chloride and carbon dioxide, samples were absorbed in standard 0.1 N sodium hydroxide. The resulting solution was titrated with standard 0.1 N nitric acid first to the phenolphthalein end-point, then to the methyl orange end-point. This determination permitted the calculation of the number of moles of hydrogen chloride and the number of moles of carbon dioxide present in the gas mixture. To determine isobutylene, samples were absorbed in standard 0.1 N bromine in potassium bromide solution. Excess potassium iodide was added, and the liberated iodine was titrated with standard sodium thiosulphate solution. This permitted a calculation of the number
of moles of isobutylene present in samples of the gas. The results are expressed as moles of each gas obtained per mole of chlorocarbonate decomposing. Results were as follows:

<table>
<thead>
<tr>
<th>Gas</th>
<th>Moles of Gas Obtained</th>
<th>Moles of Chlorocarbonate</th>
<th>Moles of Gas Per Moles of Chlorocarbonate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>.001141</td>
<td>.001135</td>
<td>1.005</td>
</tr>
<tr>
<td>Dioxide</td>
<td>.001333</td>
<td>.001344</td>
<td>.992</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>average = .999</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>.001113</td>
<td>.001135</td>
<td>.981</td>
</tr>
<tr>
<td>Chloride</td>
<td>.001323</td>
<td>.001344</td>
<td>.985</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>average = .983</td>
</tr>
<tr>
<td>Isobutylene</td>
<td>.001472</td>
<td>.001499</td>
<td>.981</td>
</tr>
<tr>
<td></td>
<td>.001384</td>
<td>.001399</td>
<td>.989</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>average = .985</td>
</tr>
</tbody>
</table>
DISCUSSION OF RESULTS
DI-TERTIARY BUTYL CARBONATE

Preparation.
The reaction between gaseous phosgene and excess sodium tertiary butylate suspended in dioxane proceeds smoothly to give di-tertiary butyl carbonate. Washing the reaction mixture with ice water removes the solvent and excess reactants almost completely. The crude product obtained may be readily purified by vacuum distillation. A yield of 40.5 percent was obtained by this method.

Stability.
Di-tertiary butyl carbonate was found to be an extremely unreactive, stable compound. It can be distilled repeatedly at 158°C. with no decomposition. Complete saponification is achieved only after heating in the presence of barium chloride for nine hours at 170°C. This is unusual, since most esters will not survive far less rigorous conditions of saponification. The compound failed to react with phenyl hydrazine when heated at 175°C to 185°C. for 172 hours. Again, this is surprising since other alkyl carbonates will react with this reagent at much lower temperatures and shorter
periods of time. Recovery of the unchanged di-tertiary butyl carbonate from this mixture indicated that the compound was not decomposed appreciably at temperatures up to 185°C.

The possibility that di-tertiary butyl carbonate is unstable was raised by Erickson and Ashton (30), who prepared di-tertiary butyl ether from silver carbonate and tertiary butyl chloride. In view of the fact that the carbonate has been found to be a highly stable compound, it seems unlikely that it occurred as an intermediate in the preparation of the ether, and therefore some other mechanism to explain the formation of the ether by this method is necessary.
DISCUSSION OF RESULTS
TERTIARY BUTYL CHLOROCARBONATE

Preparation.

Attempts to prepare tertiary butyl chlorocarbonate from the alcohol and phosgene alone indicated that no reaction would take place under these conditions. This is not surprising, because in the preparation of a number of other chlorocarbonates it is necessary to add an acid binding agent such as the tertiary amine. Attempts to prepare tertiary butyl chlorocarbonate using quinoline or dimethyl aniline as the acid binding agent resulted in some type of reaction, indicated by the precipitation of the amine hydrochloride, but yielded no trace of the chlorocarbonate. Experiments with the chlorocarbonate after it was prepared in another way explained this difficulty. Tertiary butyl chlorocarbonate reacts readily at 0° to 10°C. with dimethyl aniline, quinoline, pyridine, and triethyl amine to produce the corresponding amine hydrochloride. Apparently these amines have sufficient affinity for hydrogen chloride to cause a decomposition of the chlorocarbonate to yield this product. For this reason, methods of preparation involving the use of tertiary amines are not applicable to the production of tertiary butyl chlorocarbonate.
The reaction of sodium tertiary butylate and phosgene proceeds readily to yield the chlorocarbonate when conducted at temperatures below 0°C. Since the chlorocarbonate begins to decompose appreciably somewhere between 0°C and room temperature, it is obvious that the methods of operation are restricted to those permitting the removal of all impurities at low temperatures. These operations are made more difficult by the fact that tertiary butyl chlorocarbonate is extremely sensitive to moisture. All variations in the methods of preparation were made in attempts to find a procedure involving the least number of operations, all of which can be performed at temperatures below the point where the chlorocarbonate decomposed. Normal butane was finally selected as a solvent which can be used in liquid form but which has a low enough boiling point to permit its removal at temperatures below 0°C.

The removal of colloidal sodium chloride involved an operation which proved to be quite troublesome. In early preparations, filtration was so slow that appreciable hydrolysis of the product by atmospheric moisture occurred. The use of crystalline silica as a filter aid permitted filtration which was rapid enough to avoid this difficulty. Further to assure anhydrous conditions, the filtrations were conducted under a stream of dried methane.
A vacuum distillation procedure, which maintained both liquid and vapor at low temperatures was adopted. By this procedure, the chlorocarbonate could be boiled at 3° to 4°C., at 0.9 to 1.7 mm. This prevented thermal decomposition of the product during purification.

The final purification of the chlorocarbonate required the removal of tertiary butyl alcohol. Experiments showed that the alcohol could remain in contact with the chlorocarbonate for protracted periods of time without change. Three compounds were used in attempts to remove the alcohol by chemical reaction. Phosphorus pentoxide and sulfuryl chloride were effective in definitely improving the purity of the chlorocarbonate, but neither was as satisfactory as thionyl chloride. Experiments conducted on the reaction of thionyl chloride and tertiary butyl alcohol at -20°C. indicated that only hydrogen chloride, sulfur dioxide, and tertiary butyl chloride were formed. Since the analysis was not quantitative, it is possible that small traces of other compounds may have been produced by this reaction. Treatment with thionyl chloride did not produce pure samples of chlorocarbonate. The presence of an unsaturated hydrocarbon after this treatment, was demonstrated by the absorption of liquid bromine. Since this impurity could not be removed by distillation, its boiling point must have been close to that of the chlorocarbonate. It is suspected that the impurity was diisobutylene (boiling
point, 101.2° to 104.5°C.) (75), but this compound occurred in such small quantities that it was not isolated. Bromination so decreased its volatility that subsequent distillation separated the product from this impurity.

The combined processes described above were necessary to produce a pure sample of chlorocarbonate. The best yield obtained was 20.4 percent. The low figure may be partially explained by the formation of relatively large amounts of di-tertiary butyl carbonate during the preparation of the chlorocarbonate. This by-product was identified by melting point, but no attempt was made to isolate it quantitatively and determine its yield. Its formation is explained by the lack of instantaneous mixing during the addition of the alcoholate to the phosgene solution.

**Derivatives.**

The formation of nitrogen substituted urethanes from tertiary butyl chlorocarbonate and the corresponding amine takes place much more readily than the formation of the same urethanes from tertiary butyl alcohol and the corresponding isocyanate. One known derivative, tertiary butyl N-phenyl carbamate, and one new compound, tertiary butyl N-para-tolyl carbamate, were prepared in this manner.

**Decomposition Products.**

According to the mechanisms of chlorocarbonate
decompositions proposed by Compere (21), those chloro-
carbonates which have one or more hydrogen atoms attached
to the alpha-carbon atom in the alkyl group are the
only ones which can yield the alkyl halide upon decom-
position. Since tertiary butyl chlorocarbonate has no
alpha-hydrogen, according to the proposed mechanism no
tertiary butyl chloride should be obtained. Analysis
of the thermal decomposition products of this chloro-
carbonate indicates that no tertiary butyl chloride
is obtained. The only products identified were iso-
butylene, hydrogen chloride, and carbon dioxide.
Quantitative analysis shows that these gases account
for substantially all the chlorocarbonate decomposing.

According to present indications, the decomposition
of tertiary butyl chlorocarbonate may be represented
completely by the equation:

\[(\text{CH}_3)_3\text{COCl} \rightarrow (\text{CH}_3)_2\text{CH} = \text{CH}_2 + \text{HCl} + \text{CO}_2\]

Since this decomposition is thus far in accord
with the proposed mechanism for the decomposition of
other alkyl chlorocarbonates, a tentative mechanism
may be postulated for the decomposition of tertiary
butyl chlorocarbonate.

The configuration proposed by Compere (21) for
isopropyl chlorocarbonate which results in the produc-
tion of propylene, hydrogen chloride, and carbon
dioxide is one in which the chlorine atom rests between
the two methyl groups attached to the central carbon
atom in the isopropyl group. Since in tertiary butyl chlorocarbonate there are three methyl groups attached to the central carbon atom, any approach of the chlorine atom to the alkyl group will result in such a configuration. When decomposition occurs, this configuration can result only in the production of hydrogen chloride. The proposed configuration and mechanism of decomposition are shown in Figure I.

Complete kinetics of the decomposition of tertiary butyl chlorocarbonate will be studied at a later date. It is hoped that such study will be advantageous in explaining completely the mechanism by which chlorocarbonates decompose to give an unsaturated hydrocarbon, hydrogen chloride, and carbon dioxide.
PROPOSED MECHANISM OF DECOMPOSITION

\[(\text{CH}_3)_3\text{CO COC}_1\]

\[
\begin{align*}
\text{H}_2\text{C} & \text{H}_2\text{C} \\
\text{H} & \text{H} \quad \text{H} & \text{H} \\
\text{C} & \text{C} & \text{C} & \text{C} \quad \text{H} & \text{H} \\
\text{O} & \text{O} \\
\text{C} & \text{C} & \text{C} & \text{C} \quad \text{H} & \text{H} \\
\text{H} & \text{H} \quad \text{H} & \text{H} \\
\text{C} & \text{C} & \text{C} & \text{C} \quad \text{H} & \text{H} \\
\text{O} & \text{O} \\
\text{C} & \text{C} & \text{C} & \text{C} \quad \text{H} & \text{H} \\
\end{align*}
\]

\[(\text{CH}_3)_2\text{C} = \text{CH}_2 + \text{HCl} + \text{CO}_2\]

FIG. I
SUMMARY

Di-tertiary butyl carbonate was prepared by the reaction of gaseous phosgene with a suspension of sodium tertiary butylate in dioxane. This compound has been characterized. It was found to be a remarkably unreactive, stable ester. It is not decomposed at temperatures under 185°C. It may be saponified only with difficulty, and does not react with ammonia or phenyl hydrazine.

Tertiary butyl chlorocarbonate was prepared by the reaction of sodium tertiary butylate with a solution of phosgene in n-butane at -60°C. The reaction was also conducted in three other solvents, and a variety of methods of purification were investigated. The most successful method of purification consisted of low temperature vacuum distillation and treatment with thionyl chloride and liquid bromine. This chlorocarbonate is hydrolyzed with extreme ease and begins to decompose thermally at about 10°C.

Quantitative analysis of the gaseous products of decomposition of tertiary butyl chlorocarbonate indicates that one mole each of carbon dioxide, hydrogen chloride, and isobutylene are produced by each mole of 45.
chlorocarbonate that decomposes. No evidence of the existence of any other decomposition product was found. Indications are that the decomposition of this chlorocarbonate is in accord with the mechanisms of decomposition that have been proposed for other chlorocarbonates. A tentative mechanism for the decomposition of tertiary butyl chlorocarbonate has been advanced.
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## APPENDIX

### Preparation and Purification of Tertiary Butyl Chloroearbonate, \( \text{C}_4\text{H}_9\text{CO}_2\text{Cl} \)

<table>
<thead>
<tr>
<th>RUN NO.</th>
<th>TEMP. OF REACTION</th>
<th>SOLVENT</th>
<th>ALCOHOLATE</th>
<th>SODIUM CHLORIDE REMOVAL</th>
<th>METHOD OF PURIFICATION</th>
<th>ASSAY, PERCENT ( \text{C}_4\text{H}_9\text{CO}_2\text{Cl} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-a</td>
<td>(0-15^\circ\text{C.})</td>
<td>Benzene</td>
<td>Benzene Suspension</td>
<td>Ice Water Washed</td>
<td>None</td>
<td>0</td>
</tr>
<tr>
<td>1-b</td>
<td>(0-15^\circ\text{C.})</td>
<td>Benzene</td>
<td>Benzene Suspension</td>
<td>Filtered Through Fritted Glass</td>
<td>None</td>
<td>0</td>
</tr>
<tr>
<td>1-c</td>
<td>(0-15^\circ\text{C.})</td>
<td>Benzene</td>
<td>Benzene Suspension</td>
<td>Filtered Through Fritted Glass</td>
<td>Distilled at 1.5 mm., 30(^\circ\text{C.})</td>
<td>0</td>
</tr>
<tr>
<td>1-d</td>
<td>(0-12^\circ\text{C.})</td>
<td>Benzene</td>
<td>Benzene Suspension</td>
<td>Filtered Through Fritted Glass</td>
<td>Recrystallized from Ether</td>
<td>0</td>
</tr>
<tr>
<td>1-e</td>
<td>(0-15^\circ\text{C.})</td>
<td>Benzene</td>
<td>Benzene Suspension</td>
<td>Filtered Through Amorphous Silica Bed</td>
<td>Distilled at 110 mm.</td>
<td>0</td>
</tr>
<tr>
<td>2-a</td>
<td>(0-15^\circ\text{C.})</td>
<td>Dioxane</td>
<td>Dioxane Suspension</td>
<td>Ice Water Washed</td>
<td>None</td>
<td>0</td>
</tr>
<tr>
<td>2-b</td>
<td>(0-15^\circ\text{C.})</td>
<td>Dioxane</td>
<td>Dioxane Suspension</td>
<td>Ice Water Washed</td>
<td>None</td>
<td>0</td>
</tr>
<tr>
<td>3-a</td>
<td>-40(^\circ\text{C.})</td>
<td>Ether</td>
<td>Dry Powder</td>
<td>Filtered Through Amorphous Silica Bed</td>
<td>(Crystallized at -65(^\circ)) (Recrystallized from Ethyl Bromide) (Recrystallized from Ether-Petroleum Ether)</td>
<td>51.8</td>
</tr>
</tbody>
</table>

---

Note: The table contains information on the preparation and purification of tertiary butyl chloroearbonate, including the temperature of the reaction, the solvent used, the alcoholate, the method of sodium chloride removal, and the method of purification. The assay percent of the compound \( \text{C}_4\text{H}_9\text{CO}_2\text{Cl} \) is also provided for each run.
<table>
<thead>
<tr>
<th>RUN NO.</th>
<th>TEMP. OF REACTION</th>
<th>SOLVENT</th>
<th>ALCHEMOLATE</th>
<th>SODIUM CHLORIDE REMOVAL</th>
<th>METHOD OF PURIFICATION</th>
<th>ASSAY, PERCENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-b</td>
<td>-45°C</td>
<td>Ether</td>
<td>Dry Powder</td>
<td>Filtered Through Amorphous Silica Bed</td>
<td>Reerystallised from Ether-Petroleum Ether</td>
<td>68.9</td>
</tr>
<tr>
<td>4</td>
<td>-45°C</td>
<td>None</td>
<td>Dry Powder</td>
<td>Filtered Through Amorphous Silica Bed</td>
<td>Reerystallised at -65°C.</td>
<td>48.0</td>
</tr>
<tr>
<td>5-a</td>
<td>-60°C</td>
<td>Ethyl Chloride</td>
<td>Dry Powder</td>
<td>Filtered Through Amorphous Silica Bed</td>
<td>Reerystallised at -65°C.</td>
<td>63.0</td>
</tr>
<tr>
<td>5-b</td>
<td>-60°C</td>
<td>Ethyl Chloride</td>
<td>Dry Powder</td>
<td>Centrifuged</td>
<td>Reerystallised at -65°C.</td>
<td>22.0</td>
</tr>
<tr>
<td>6-a</td>
<td>-60°C</td>
<td>n-Butane</td>
<td>Dry Powder</td>
<td>Filtered Through Amorphous Silica Bed</td>
<td>(t-Butyl Alcohol Crystallized, Filtered (Distilled at 3 mm.)</td>
<td>82.8</td>
</tr>
<tr>
<td>6-b</td>
<td>-60°C</td>
<td>n-Butane</td>
<td>Dry Powder</td>
<td>Filtered Through Amorphous Silica Bed</td>
<td>Treated with Phosphorus Pentoxide, Distilled at 2.5 mm.</td>
<td>81.0</td>
</tr>
<tr>
<td>6-c</td>
<td>-60°C</td>
<td>n-Butane</td>
<td>Dry Powder</td>
<td>Filtered Through Super Cel Bed</td>
<td>Treated with Phosphorus Pentoxide Before and After Butane Removal, Distilled (Three Distillations at 2 mm.)</td>
<td>94.5</td>
</tr>
<tr>
<td>RUN NO.</td>
<td>TEMP. OF REACTION</td>
<td>SOLVENT</td>
<td>ALCOHOLATE</td>
<td>SODIUM CHLORIDE REMOVAL</td>
<td>METHOD OF PURIFICATION</td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>------------------</td>
<td>---------</td>
<td>------------</td>
<td>-------------------------</td>
<td>------------------------</td>
<td></td>
</tr>
<tr>
<td>6-d</td>
<td>-60°C</td>
<td>n-Butane</td>
<td>Dry Powder</td>
<td>Filtered Through Super Cel Bed</td>
<td>Treated with Phosphorus Pentoxide Before and After Butane Removal, Distilled (one distillation at 2 mm.)</td>
<td></td>
</tr>
<tr>
<td>6-e</td>
<td>-60°C</td>
<td>n-Butane</td>
<td>Dry Powder</td>
<td>Filtered Through Super Cel Bed</td>
<td>Treated with Phosphorus Pentoxide, Distilled (Two Distillations at 2 mm.)</td>
<td></td>
</tr>
<tr>
<td>6-f</td>
<td>-60°C</td>
<td>n-Butane</td>
<td>Dry Powder</td>
<td>Filtered Through Super Cel Bed</td>
<td>Distilled at 2 mm.</td>
<td></td>
</tr>
<tr>
<td>6-g</td>
<td>-60°C</td>
<td>n-Butane</td>
<td>Dry Powder</td>
<td>Filtered Through Super Cel Bed</td>
<td>(Distilled (three distillations at 2mm.) (Treated with Thionyl Chloride, Distilled (Two Distillations at 2 mm.), 97.8</td>
<td></td>
</tr>
<tr>
<td>6-h</td>
<td>-60°C</td>
<td>n-Butane</td>
<td>Dry Powder</td>
<td>Filtered Through Super Cel Bed</td>
<td>Distilled (Two Distillations at 2 mm.), Treated with Thionyl Chloride Twice</td>
<td>91.00</td>
</tr>
</tbody>
</table>

ASSAY, PERCENT C<sub>4</sub>H<sub>9</sub>CO₂Cl

85.1
85.6
89.8
85.0
97.8
91.00
<table>
<thead>
<tr>
<th>RUN NO.</th>
<th>TEMP. OF REACTION</th>
<th>SOLVENT</th>
<th>ALCOHOLATE</th>
<th>SODIUM CHLORIDE REMOVAL</th>
<th>METHOD OF PURIFICATION</th>
<th>ASSAY, (\text{C}_4\text{H}_7\text{CO}_2\text{Cl}) PERCENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-i</td>
<td>-60°C.</td>
<td>n-Butane</td>
<td>Dry Powder</td>
<td>Filtered Through Bed of Super Cel and Silica</td>
<td>Treated with Thionyl Chloride twice</td>
<td>92.00</td>
</tr>
<tr>
<td>6-j</td>
<td>-60°C.</td>
<td>n-Butane</td>
<td>Dry Powder</td>
<td>Filtered Through Bed of Super Cel and Silica</td>
<td>Treated with Thionyl Chloride</td>
<td>80.6</td>
</tr>
<tr>
<td>6-k</td>
<td>-60°C.</td>
<td>n-Butane</td>
<td>Dry Powder</td>
<td>Filtered Through Silica Bed</td>
<td>Distilled (Two Distillations at 2 mm.), Treated with Thionyl Chloride</td>
<td>82.9</td>
</tr>
<tr>
<td>6-l</td>
<td>-60°C.</td>
<td>n-Butane</td>
<td>Dry Powder</td>
<td>Filtered Through Silica Bed</td>
<td>Distilled at 2 mm.</td>
<td>89.1</td>
</tr>
<tr>
<td>6-m</td>
<td>-60°C.</td>
<td>n-Butane</td>
<td>Dry Powder</td>
<td>Filtered Through Silica Bed</td>
<td>Treated with Thionyl Chloride, Distilled (Two Distillations at 2 mm.)</td>
<td>98.0</td>
</tr>
<tr>
<td>6-n</td>
<td>-60°C.</td>
<td>n-Butane</td>
<td>Dry Powder</td>
<td>Filtered Through Silica Bed</td>
<td>Treated with Sulfuryl Chloride, Distilled at 2 mm.</td>
<td>96.0</td>
</tr>
<tr>
<td>6-o</td>
<td>-60°C.</td>
<td>n-Butane</td>
<td>Dry Powder</td>
<td>Filtered Through Silica Bed</td>
<td>Treated with Thionyl Chloride and Bromine Twice, Distilled at 2 mm.</td>
<td>99.3</td>
</tr>
</tbody>
</table>
VITA

James Wesley Rogers was born in Arkadelphia, Arkansas, on August 29, 1919. Elementary education was received in the grammar schools of El Dorado and Smackover, Arkansas, and in Branham and Hughes Military Academy, Spring Hill, Tennessee. He was graduated from El Dorado High School in May, 1936.

The following September, he entered El Dorado Junior College where he was enrolled for two years. In September, 1938, he entered Hendrix College and was graduated with the Bachelor of Arts degree in June, 1940.

In September, 1940, he entered Louisiana State University with an appointment as teaching fellow in the Department of Chemistry. In August, 1942, he received the Master of Science Degree from this department.

He was appointed Instructor in Chemistry in September, 1943. He is now a candidate for the degree of Doctor of Philosophy in Chemistry.
EXAMINATION AND THESIS REPORT

Candidate: James Wesley Rogers

Major Field: Chemistry

Title of Thesis: The Preparation, Characterization, and Thermal Decomposition Products of Di-Tertiary Butyl Carbonate and Tertiary Butyl Chlorocarbonate

Approved:

[Signatures]

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

EXAMINEE:

[Signatures]

Date of Examination: July 30, 1947

[Signatures]