Conversion of Bis(trichloromethyl) Carbonate to Phosgene and Reactivity of Triphosgene, Diphosgene, and Phosgene with Methanol[1]

Lucia Pasquato,*[,†] Giorgio Modena,[†] Livius Cotarca,*[,‡,§] Pietro Delogu,[‡] and Silvia Mantovani[‡]

Centro CNR Meccanismi di Reazioni Organiche[†] and Dipartimento di Chimica Organica Università di Padova, via Marzolo 1, 35131 Padova, Italy, and Industrie Chimiche Caffaro SpA,[‡] Centro Ricerche Torviscosa, P-le F. Marinotti 1, 33050 Torviscosa Udine, Italy

pasquato@chor.unipd.it

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Triphosgene was decomposed quantitatively to phosgene by chloride ion. The reaction course was monitored by IR spectroscopy (React-IR), showing that diphosgene was an intermediate. The methanolysis of triphosgene in deuterated chloroform, monitored by proton NMR spectroscopy, gave methyl chloroformate and methyl 1,1,1-trichloromethyl carbonate in about a 1:1 ratio, as primary products. The reaction carried out in the presence of large excess of methanol (0.3 M, 30 equiv) was a pseudo-first-order process with a k_{obs} of 1.0×10^{-4} s^{-1}. Under the same conditions, values of k_{obs} of 0.9×10^{-3} s^{-1} and 1.7×10^{-2} s^{-1} for the methanolysis of diphosgene and phosgene, respectively, were determined. The experimental data suggest that, under these conditions, the maximum concentration of phosgene during the methanolysis of triphosgene and diphosgene was lower than 1×10^{-5} M. Methyl 1,1,1-trichloromethyl carbonate was synthesized and characterized also by the APCI-MS technique.

In the past decade there has been a growing interest in the use of triphosgene (bis(trichloromethyl) carbonate or BTC) in organic synthesis. Its properties as well as the synthetic application have been recently reviewed.[2] The very large number of patents with respect to the cumulative number of papers found in Chemical Abstracts (85% in 1996) shows the industrial relevance of this reagent.[3] The main reason for such intensive application of BTC in synthesis may be ascribed to two different aspects, namely: (i) the use of triphosgene as a safer solid and easier to handle compared to phosgene[4,5] and (ii) the specific reactivity of triphosgene that enables the preparation of unsymmetrical ureas,[6] carbamoyl chlorides and isocyanates,[7] unsymmetrical carbonates,[8] and carbamates.[9] Regarding the first aspect, a central point is to understand if, and under what conditions, triphosgene releases phosgene and consequently how triphosgene can be used safely. Regarding the second aspect there are two key points to examine: the mechanism of action of triphosgene toward nucleophiles both in the presence and in the absence of catalysts and if during these reactions phosgene is formed in harmless quantities.

Our interest in the chemistry of triphosgene (**1**) has prompted us to investigate the depolymerization of triphosgene in the presence of chloride ions.[10] Particularly interesting was monitoring the process continuously using the instrument React-IR since it revealed the presence of diphosgene (**2**) as an intermediate and hence allows the mechanism of the process to be understood. Furthermore, we investigated the reaction of triphosgene (**1**) with methanol (as a model for a weak nucleophile) in the presence, as well as in the absence, of chloride ions. For comparison we studied the same reaction with diphosgene (**2**) and phosgene (**3**). Preliminary data, obtained by monitoring the reactions with proton NMR spectra, clearly showed that phosgene is the most reactive species. In addition, on the basis of the experimental data, we may propose a mechanism for the methanolysis

[†] CMRO-CNR, University of Padova.

[‡] Industrie Chimiche Caffaro.

[§] Current address: Zambon Group SpA, Centro Ricerche, 36045 Almisano di Lonigo (VI), Italy. e-mail: livius.cotarca@zambongroup.com.

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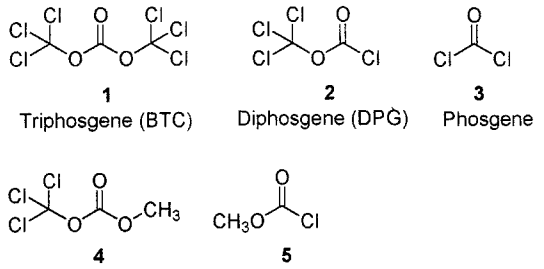
Chart 1



of triphosgene that is also a rationalization for the formation of unsymmetrical carbonates or ureas. Finally, an efficient synthesis of the methyl 1,1,1-trichloromethyl carbonate (**4**), which is a primary product in the methanolysis of triphosgene and diphosgene, and complete characterization are reported.

Results and Discussion

Conversion of Triphosgene to Phosgene by Chloride Ions. We carried out several experiments of decomposition of triphosgene (**1**) in different solvents or undiluted using catalytic amounts of tetrabutylammonium salts (5−10% w/w), to determine the products of the reaction and the stoichiometry of the process. In addition, some of these reactions have been monitored by means of the mobile probe of the instrument React-IR-MP, which records several IR spectra per minute and allows statistical analysis of the spectroscopic data. In a typical experiment a solution of triphosgene in *n*-hexane (10% w/w) was treated with Aliquat 336 (3 mol % vs triphosgene) added at one time, and the reaction, carried out at room temperature, was monitored with the system React-IR.

The spectroscopic data definitely indicate the presence of three detectable species: the reagent, triphosgene (**1**); the product, phosgene (**3**); and an intermediate. A detailed and careful analysis of the IR spectra allows the identification of the absorption bands pertaining undoubtedly to diphosgene (**2**). The profiles reported in Figure 1 represent the variation of absorbance vs time for triphosgene ($\nu = 1177$ cm^{-1}), phosgene ($\nu = 836$ cm^{-1}), and diphosgene ($\nu = 1054$ cm^{-1}). In Figure 1 the absorbance of diphosgene changes as expected for a reactive intermediate which builds up at early stages of the reaction and then decreases.

The phosgene produced during the process was condensed into a methanol solution at −12 °C. This solution, at the end of the reaction, was subjected to quantitative analysis to determine the dimethyl carbonate formed. Indeed, the reaction is quantitative, and three equivalents of dimethyl carbonate were formed per mole of triphosgene.

The above experimental evidence points to the mechanism outlined in Scheme 1, centered on the nucleophilic role of the chloride ion.

The chloride ion, under these reaction conditions, is a strong nucleophile that attacks the carbonyl carbon of triphosgene giving diphosgene and phosgene. In turn, diphosgene reacts with chloride ion to give two molecules of phosgene. The chloride ion is needed in catalytic amount since it is not consumed in the overall process.

The results outlined above suggest that phosgene can be used safely by producing it in desired quantities from triphosgene, using a catalytic amount of chloride ions (3−5%) in a flask directly connected to the reaction vessel where the phosgene is needed as a reagent. In this respect we can confirm that *triphosgene is a solid phosgene equivalent*.

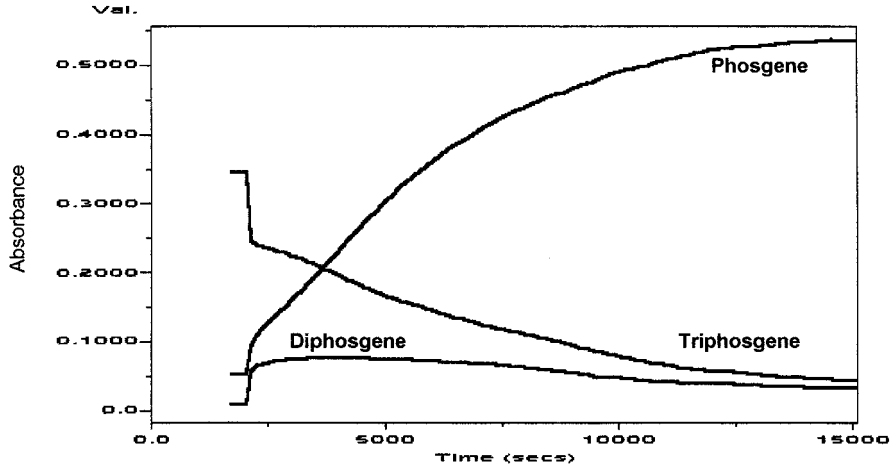
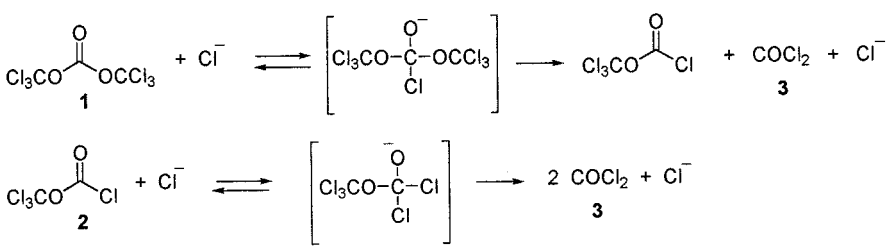


Figure 1. Absorbance vs time (s) as monitored by React-IR in the Aliquat (3%) catalyzed conversion of triphosgene (11% w/w) to phosgene carried out in *n*-hexane at room temperature.

Scheme 1



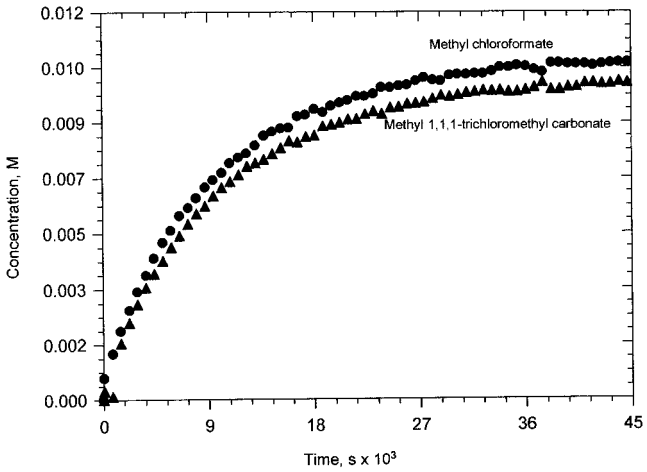


Figure 2. Reaction of triphosgene (0.01 M) with methanol (0.3 M) in $CDCl_3$ at 25 °C.

Reactions of Triphosgene, Diphosgene, and Phosgene with Methanol. We carried out two sets of experiments, both in the absence of catalyst and in the presence of chloride ions (added as tetrabutylammonium chloride). All the reactions were carried out in deuterated chloroform (freshly distilled before use) in the presence of an excess of methanol (0.3 M, 30 equiv) at 25 °C in screw cap NMR tubes, and they were monitored by proton NMR (400 MHz, ^{1}H selective probe) at appropriate regular intervals.

The reaction of triphosgene with methanol forms a mixture, one to one, of methyl 1,1,1-trichloromethyl carbonate[11] (**4**) and methyl chloroformate (**5**) as reported in an earlier mechanistic study.[4,12] Only with a very long reaction time (several days) was dimethyl carbonate obtained as a final product.[13] The formation of products **4** and **5** was followed by integration of the corresponding singlets at 3.941 and 3.948 ppm, respectively, and the small difference to the one-to-one ratio is likely due to the integration error due to imperfect resolution of the two peaks. A typical profile of concentration vs time is reported in Figure 2. The pseudo first-order rate constant for this reaction is reported in Table 1.

The reaction of diphosgene (**2**) (0.01 M) with 30 equiv of methanol in chloroform gives a mixture of methyl 1,1,1-trichloromethyl carbonate (**4**) and methyl chloroformate (**5**) in a 8.8 to 3.2 ratio. A typical profile of this reaction is reported in Figure 3, and the relative pseudo-first-order rate constant is reported in Table 1.

Phosgene (0.01 M) reacts with 30 equiv of methanol, giving methyl chloroformate as the only product. The reaction is very fast at 25 °C, and the estimate pseudo-first-order rate constant is reported in Table 1.

Under the same conditions but in the presence of small quantities of tetrabutylammonium chloride (0.5×10^{-3} M and 1×10^{-3} M), we monitored the reactions of triphosgene, diphosgene, and phosgene with methanol (0.3 M, 30 equiv). In the first two cases the formation of the products shows the same qualitative behavior observed in the processes carried out in the absence of chloride ions. In addition, we could not detect any appreciable difference using 5% or 10% of chloride ion. The pseudo-first-order rate constants for these reactions are reported in Table 1. As the reaction of phosgene, under these conditions, is too fast (it goes to completion in the mixing time), we could not determine the rate constant for this process.

Table 1. Pseudo-First-Order Rate Constants for the Reactions of Phosgene, Diphosgene, and Triphosgene (0.01 M) with Methanol (0.3 M) in $CDCl_3$ at 25 °C, Calculated from the Initial Rates

substrate	k_{obs}, s^{-1} MeOH, 0.3 M	MeOH, 0.3 M, Cl^- 5%[a]	MeOH, 0.3 M, Cl^- 10%[a]
phosgene	1.7×10^{-2}	*b*	*b*
diphosgene	9.1×10^{-4}	1.0×10^{-3}	1.1×10^{-3}
triphosgene	1.0×10^{-4}	2.3×10^{-4}	2.3×10^{-4}

[a] Added as $Bu_4N^+Cl^-$. [b] Too fast to be measured by NMR.

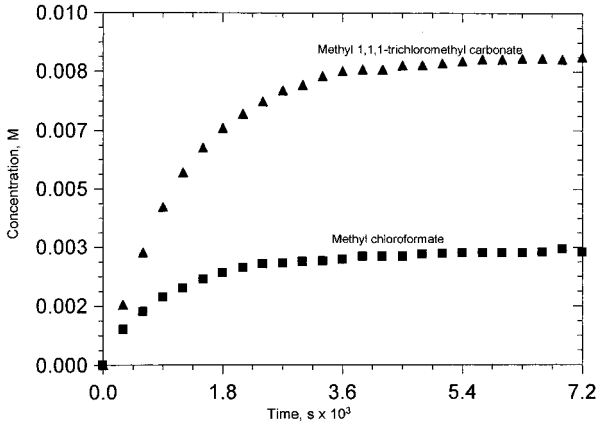


Figure 3. Reaction of diphosgene (0.01 M) with methanol (0.3 M) in $CDCl_3$ at 25 °C.

On the basis of the experimental data presented for the methanolysis of triphosgene, we can suggest for this process the reaction sequence shown in Scheme 2. The rate-determining step is probably the formation of a tetrahedral intermediate or transition state, which then gives the methyl 1,1,1-trichloromethyl carbonate and phosgene. In turn, phosgene reacts with methanol to give methyl chloroformate. Since this last reaction is much faster than the rate-determining step, *under these conditions phosgene will not accumulate*. This is supported by the fitting[14] of the process using the differential equations relative to the reactions reported in Scheme 2 which indicate a maximum concentration of phosgene of 1×10^{-5} M.

The data obtained for the methanolysis of diphosgene are in agreement with the mechanistic picture reported in Scheme 3.

Diphosgene reacts with methanol to form a tetrahedral intermediate, which has two good leaving groups: the chloride ion and the trichloromethoxy groups. The loss of the former gives methyl 1,1,1-trichloromethyl carbonate whereas the detachment of the latter leads to methyl

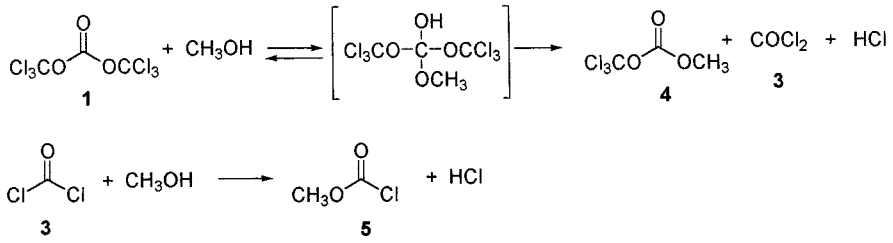
(11) Compound **4** is know; however, we could not find in the literature its spectroscopic data since its preparation is described only in ref 15. This is the reason we report its complete characterization in the next section.

(12) Cotarca, L.; Bacaloglu, R.; Marcu, N.; Tarnaveanu, A. *J. Prakt. Chem.* **1985**, *327*, 881.

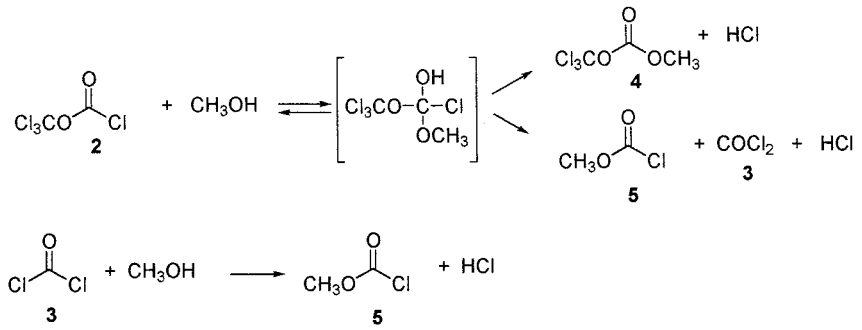
(13) Methyl chloroformate and methyl 1,1,1-trichloromethyl carbonate react very slowly under the reaction conditions used for the methanolysis of triphosgene. Only 10% of compound **5** (0.01M) with 20 equiv of methanol and 18 equiv of 2,6-di-*tert*-butylpyridine (to speed up the reaction) is consumed in 14 h, giving 2 equiv of dimethyl carbonate. Under the same reaction conditions, methyl chloroformate (**5**) reacts faster; about 20% is consumed in the same time course, giving 1 equiv of dimethyl carbonate.

(14) The program Scientist, MicroMath Scientific Software, was used.

Scheme 2



Scheme 3



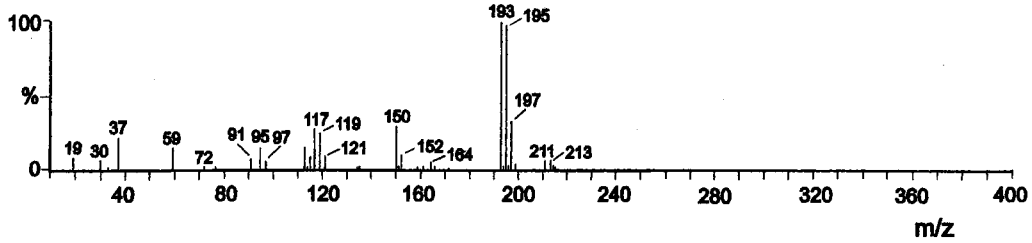


Figure 4. APCI-MS spectrum of methyl 1,1,1-trichloromethyl carbonate.

chloroformate and phosgene which in turn again gives methyl chloroformate. Therefore, the lability of the groups is reflected in the ratio between product **4** and half of product **5**, which is about 5. In this case, also, phosgene should be present during the reaction as an intermediate with a quite low maximum concentration in solution. Indeed, the fitting of the experimental data allows estimation of a maximum phosgene concentration smaller than 3×10^{-6} M.

As indicated in Schemes 2 and 3, 2 equiv of hydrogen chloride are formed in the methanolysis of triphosgene and diphosgene. This should suggest that even using 30 equiv of methanol one would observed an inhibition due to the solvation of HCl by the methanol (each HCl would sequester no less than three molecules of methanol). Higher methanol concentration and constant ionic strength would obviate this complication. We did not take this precaution mainly because of the limitations dictated by the NMR technique used to monitor the process. However, as a first approximation, the concentration vs time in all the experiments carried out follows pseudo-first-order behavior up to 80% of the reaction.

The methanolysis reaction carried out in the presence of small quantities of chloride ions added as tetrabutylammonium chloride are indicative of the weak effect of chloride ion as base and the lack of any nucleophilic role played by chloride ions. Indeed, as shown by the data reported in Table 1, the reactions carried out in the presence of 5% or 10% of chloride ion are very similar to those without added salt. This behavior is attributed to the formation of hydrogen chloride during the methanolysis. Thus, the presence of catalytic quantities of chloride ions may influence the initial part of the reaction, but should be a negligible factor during the progress of the process.

Synthesis and Characterization of Methyl 1,1,1-Trichloromethyl Carbonate (4). Compound **4** is known since 1887 when Hentschel[15] prepared it by reaction of diphosgene in refluxing methanol. Later, two other groups[16,17] reported the formation in small amount of **4** by chlorination of dimethyl carbonate together with other polychlorinated carbonates.

As we described above, methyl 1,1,1-trichloromethyl carbonate is formed in the methanolysis of triphosgene in chloroform. This suggested a modification of this reaction for the production of **4**. A solution of methanol (2 mL) and diisopropylethylamine (9.7 mL) in 160 mL of dry methylene chloride was slowly added to a solution of triphosgene (5 g) dissolved in 90 mL of dry methylene chloride at −10 °C. After workup, the product was separated from the crude mixture by Kulgheror distillation (75−80 °C at 15 mmHg) with an 80% yield. This lachrimatory colorless oil shows a singlet at 3.941 ppm in the proton NMR spectrum. Its ^{13}C NMR spectrum presents three signals at 56.241 ppm for the methoxy carbon, 107.702 ppm for the trichloromethoxy carbon,

(15) Hentschel, W. *J. Prakt. Chem.* **1887**, *36*, 304.
(16) Kling, A.; Florentin, D.; Jacob, E. *C. r. d l' Acad. Sci.* **1920**, *170*, 111.
(17) Grignard, V.; Rivat, G.; Urbain, E. *Ann, Chim.* **1920**, [9], t*XIII*, 229. Kling, A.; Florentin, D.; Jacob, E. *C. r. d l' Acad. Sci.* **1919**, *170*, 234.

and 148.431 ppm for the carbonyl carbon. The carbonyl IR absorbance is at 1794.7 cm^{-1}. Only operating at atmospheric pressure in air using an APCI source coupled with a quadrupolar mass analyzer could we observe the MH^+ ion (*m*/*z* 193, 195, 197 in 1:1:0.3 ratio) as the predominant species, Figure 4. The spectrum shows also an easy Cl_3C^+ loss (*m*/*z* 117, 119, 121).

Conclusions. We have reported a detailed study of the conversion of triphosgene to phosgene catalyzed by chloride ions. The experimental data indicate that triphosgene can be used as a safe synthetic equivalent of phosgene. The process we have described allows production of the desired quantity of phosgene under controlled conditions in a vessel directly connected with the reactor where the phosgene will be used.

We have also reported a thorough investigation of the methanolysis of triphosgene, diphosgene, and phosgene. The pseudo-first-order kinetic constants of these reactions carried out in the presence of excess of methanol clearly indicate that phosgene reacts more than 2 orders of magnitude faster than does triphosgene. Thus, under the reaction conditions used, phosgene does not accumulate during the methanolysis of triphosgene and its maximum concentration is always very low ($<1 \times 10^{-5}$ M). It is worth noting that both 1,1,1-trichloromethyl methyl carbonate and methyl chloroformate react with methanol at a much slower rate than triphosgene. This very different reactivity between triphosgene and the primary products formed by reaction with a nucleophile allows production of unsymmetrical carbonates and unsymmetrical ureas.

Experimental Section

General. ^{1}H NMR spectra were recorded at 200 MHz, or at 400 MHz, ^{13}C NMR at 62.9 MHz, using $CDCl_3$ as solvent. Reaction kinetics of phosgene were performed with a 200 MHz NMR instrument, and reaction kinetics of triphosgene and diphosgene were monitored using a 400 MHz (^{1}H selective probe) NMR instrument. Both instruments were equipped with a variable temperature unit, and all kinetics were performed at 25 °C. Commercial $CDCl_3$ was carefully dried before use by refluxing over P_2O_5 and then stored with A4 molecular sieves. Commercial tetrabutylammonium chloride was dried with P_2O_5 in a drying pistol. FT-IR measurements were recorded with the ReactIR-MP (Mobile Probe) system using *n*-hexane as solvent. Routine IR spectra were recorded with a FT IR Perkin-Elmer 1720 X instrument.

APCI-MS measurements were carried out on a TRIO 100 II instrument (Fisons Instruments, Manchester, UK) equipped with a Fisons APCI source. A schematic of this source and of the experimental setup used for the introduction of vaporized samples was given in an earlier paper.[18]

GC analysis of methyl chloroformate was made on a Perkin-Elmer Autosystem instrument using a 25 m capillary column of 25QC2/BPX5 and helium as carrier gas with a flux of 0.9 mL/min. Methyl chloroformate has a R_f of 4.88 min using *T*(injector) 290 °C, *T*(detector) 300 °C, 40 °C × 6 min, 20 °C/min. For quantitative determinations, dimethyl oxalate was used as a standard.

Commercial reagents were purchased from standard chemical suppliers.

(18) Donò, A.; Paradisi, C.; Scorrano, G. *Rapid Commun. Mass Spectrom.* **1997**, *11*, 1687.

Kinetic Measurements. The concentrations of tetrabutylammonium chloride, triphosgene, diphosgene, and phosgene were determined by weighing. The increases in the concentration of methyl chloroformate, 1,1,1-trichloromethyl methyl carbonate, and dimethyl carbonate were followed by measuring the ^{1}H NMR integrated area of the methyl resonances at 3.948, 3.941, and 3.640 ppm, respectively. These concentrations in $CDCl_3$ were determined by comparison of the integrated areas of appropriate resonances with that of the proton impurity of the solvent. The concentration of the impurity had been previously measured by comparison with the signal of 1,4-dinitrobenzene, at a concentration determined by weighing. The reactions have been monitored at regular time intervals, using NMR tubes equipped with airtight screw caps. At least three or four independent experiments were carried out for each reaction, and the pseudo-first-order kinetic constants reported in Table 1 are average values.

Decomposition of Triphosgene. In a typical experiment a 100 mL round-bottom flask equipped with Claisen condenser, dropping funnel, magnetic stirring, and the mobile probe of React-IR was charged with 2.1 g (7.07 mmol) of triphosgene dissolved in 20 mL of *n*-hexane. The Claisen condenser and the reactor connected with it, containing 30 mL of methanol, were kept at −12 °C. At room temperature, a solution of 0.087 g of Aliquat 336 (0.03 equiv, 0.215 mmol) dissolved in 5 mL of *n*-hexane was added dropwise under vigorous stirring to the triphosgene solution. The phosgene that developed during the reaction was collected in methanol, and the methyl chloroformate formed was quantitatively determined by GC using diethyl ether as solvent and dimethyl oxalate as standard. The IR spectra recorded during the experiment were elaborated, and a statistical analysis was carried out using the statistical software Conc-IRT.

Methyl 1,1,1-Trichloromethyl Carbonate (4).[17] A 250 mL round-bottom flask equipped with a dropping funnel, magnetic stirring bar, and condenser was charged with a solution of 5 g of BTC (0.017 mol) in 90 mL of distilled CH_2Cl_2. A solution of 9.7 mL (0.05 mol) of DIEA and 2 mL of methanol (0.05 mol) in 160 mL of distilled CH_2Cl_2 was added dropwise during 20 min, keeping the reaction vessel at −10 °C. The mixture was washed with a 10% solution of $KHSO_4$ (2 × 200 mL), a 5% solution of $NaHCO_3$ (2 × 200 mL), and finally brine (1 × 100 mL) and dried over sodium sulfate. Solvent was removed in vacuo, and the residual oil was purified by Kugelrorh distillation (75 °C, 15 mmHg). The product (2.6 g) was obtained as a colorless lachrimatory oil in 80% yield. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 3.94 (3H, s). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ: 56.241, 107.702, 148.431. FT-IR (solution 0.3 M in $CHCl_3$, cell CaF_2 0.1 mm) ν (cm^{-1}): 1797 (s), 1712 (w), 1442 (m), 1254 (s), 1194 (w), 1095 (s). MS (APCI) see Figure 4. Anal. Calcd for $C_3H_3Cl_3O_3$: C, 18.63; H, 1.56. Found: C, 18.37; H, 1.48.

Acknowledgment. We thank Prof. Cristina Paradisi and Dr. Anna Nicoletti for the mass spectra of compound **4** and Dr. Giuseppina Vassallo for the statistical analysis of IR spectra recorded with React-IR.

Supporting Information Available: The stacked plot of IR spectra recorded for a model reaction of conversion of triphosgene to phosgene catalyzed by chloride ions and the stacked plot of the proton NMR spectra of a model reaction of triphosgene (0.01 M) with methanol (0.3 M) in $CDCl_3$ at 25 °C are reported in Figure S1 and Figure S2, respectively. This material is available free of charge on the Internet at http://pubs.acs.org.

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